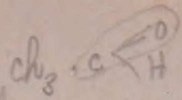
Carboxyl $COOH$

Carbonyl CO aldehydes



$ch_3 \cdot C \langle {}^{O}_{H}$

" group CHO

Digitized by the Internet Archive
in 2023 with funding from
Kahle/Austin Foundation

https://archive.org/details/organicchemistry0000herb

International Library of Technology
16D

Organic Chemistry

49 Illustrations

By
HERBERT WINKEL, B. S.
DIRECTOR, SCHOOL OF CHEMISTRY AND METALLURGY
INTERNATIONAL CORRESPONDENCE SCHOOLS

ORGANIC CHEMISTRY
(PARTS 1–7)

Published by
INTERNATIONAL TEXTBOOK COMPANY
SCRANTON, PA.
1927

Organic Chemistry, Parts 1, 2, 3, 4: Copyright, 1924, 1913, by INTERNATIONAL TEXTBOOK COMPANY.

Organic Chemistry, Parts 5, 6, 7: Copyright, 1925, 1913, by INTERNATIONAL TEXTBOOK COMPANY

Copyright in Great Britain

All rights reserved

Printed in U. S. A.

PRESS OF
INTERNATIONAL TEXTBOOK COMPANY
SCRANTON, PA.
16D

90721

PREFACE

The volumes of the International Library of Technology are made up of Instruction Papers, or Sections, comprising the various courses of instruction for students of the International Correspondence Schools. The original manuscripts are prepared by persons thoroughly qualified both technically and by experience to write with authority, and in many cases they are regularly employed elsewhere in practical work as experts. The manuscripts are then carefully edited to make them suitable for correspondence instruction. The Instruction Papers are written clearly and in the simplest language possible, so as to make them readily understood by all students. Necessary technical expressions are clearly explained when introduced.

The great majority of our students wish to prepare themselves for advancement in their vocations or to qualify for more congenial occupations. Usually they are employed and able to devote only a few hours a day to study. Therefore every effort must be made to give them practical and accurate information in clear and concise form and to make this information include all of the essentials but none of the nonessentials. To make the text clear, illustrations are used freely. These illustrations are especially made by our own Illustrating Department in order to adapt them fully to the requirements of the text.

In the table of contents that immediately follows are given the titles of the Sections included in this volume, and under each title are listed the main topics discussed.

INTERNATIONAL TEXTBOOK COMPANY

CONTENTS

NOTE.—This volume is made up of a number of separate parts, or sections, as indicated by their titles, and the page numbers of each usually begin with 1. In this list of contents the titles of the parts are given in the order in which they appear in the book, and under each title is a full synopsis of the subjects treated.

ORGANIC CHEMISTRY, PART 1

Pages
Aliphatic Series of Hydrocarbons 1–38
Introduction 1
Paraffins, or Hydrocarbons of the Methane Series 2
Methane, or Marsh Gas, CH_4 3–10
Occurrence; Properties; Composition; Reactions of methane and halogens; Substitution products; Saturated and unsaturated compounds; Structural and graphic formulas; Radicals.
Halogen Compounds of Methane 11–17
Methyl chloride; Reversible reactions; Methyl bromide and methyl iodide; Methylene iodide, chloride, and bromide; Chloroform; Iodoform; Bromoform; Carbon tetrachloride.
Ethane 18–25
Occurrence and preparation; Table of hydrocarbons of paraffin series; Ethyl chloride, bromide, and iodide.
Higher Members of the Paraffin Series 26–27
Synthesis of propane and butane; Naming of compounds; Names and formulas of hydrocarbons.
General Formulas 27
Homologous Series 28
Isomerism 28–31
Meaning of isomerism; Isomerides among paraffins.
Definitions 32–34
Classes of paraffins; Open-chain compounds; Systems of nomenclature; Names and formulas of hydrocarbons.
Reagents and Reactions 35–38
Reagents used in organic chemistry; General reactions; Completed and incompleted reactions.

ORGANIC CHEMISTRY, PART 2

Pages
Monohydroxy Alcohols 1–21
Theoretical Considerations 1– 7
Structure of alcohol; Names of alcohols; Isomeric alcohols.

General Method of Preparation and Properties....... 8
Methyl Alcohol 9–10
Ethyl Alcohol 11–13
Manufacture of alcohol; Absolute alcohol; Properties of ethyl alcohol.

Industrial Alcohol 14
Proof spirit; Denatured alcohol.

Higher Alcohols 15–18
Fusel oil; Normal propyl alcohol; Isopropyl alcohol; Butyl alcohols; Amyl alcohol; Effects of oxidation on alcohols.

Stereoisomerism 19–21
Meaning; Explanation of stereoisomerism.

Aldehydes 22–30
Structure of aldehydes; General properties; Formaldehyde; Polymerization; Acetaldehyde; Chloral, or trichloraldehyde; Aldol; Tests for aldehydes.

Ketones 31
Monobasic Acids 32–47
Properties and Structure........................ 32–34
Formic Acid 35–37
Acetic Acid 38–40
Halogen Derivatives of Acetic Acid................ 41–42
Acids and Hydrides 43
Propionic Acids 44
Higher Fatty Acids........................ 45–46
Palmitic acid; Stearic acid.

Soaps 47
Ethereal Salts, or Esters........................ 48–54
Properties and formation; Esters of inorganic acids; Esters of organic acids; Hydrolysis and saponification.

Ethers 55–58
Sulphur Derivatives 58–62
Structure; General methods of preparation; General properties; Mercaptides; Sulphur ethers; Sulphonic acids.

ORGANIC CHEMISTRY, PART 3

Pages
Derivatives of Saturated Aliphatic Hydrocarbons..... 1–24
Alkyl Compounds of Nitrogen...................... 1–20
Alkyl Amines or Substituted Ammonias............ 1– 6
Nitro Compounds 7– 8
Cyanogen and Its Compounds...................... 9–11
Halogen Compounds of Cyanogen................. 12
Cyanogen Acids and Salts........................ 13
Cyanuric acid; Isocyanic acid; Isomerism of cyanic acids; Thiocyanic acid.
Alkyl Cyanides or Nitriles....................... 14–15
Structure; Methyl and ethyl cyanides.
Alkyl Isocyanides or Carbylamines................ 16
Cyanates and Isocyanates......................... 17–18
Thiocyanates 19
Isothiocyanates 20
Alkyl Compounds of Metals and Non-Metals......... 21–23
Organo-Metallic Compounds........................ 21–22
Organo-Nonmetallic Compounds 23
Unsaturated Hydrocarbons of the Aliphatic Series.... 24–32
Ethylene, or Olefine, Series...................... 24–29
Structure; General properties; Members of the olefine series.
Acetylene Series 30–32
Structure and preparation; Relationship between compounds.
Compounds of Greater Unsaturation............... 32
Formations; Diethylenes; Diallyl; Dipropargyl.
Derivatives of Unsaturated Aliphatic Hydrocarbons.. 33–58
Derivatives of Ethylene Series................... 33–41
Vinyl chloride; Allyl chloride, bromide, and sulphide; Allyl cyanides; Allyl isothiocyanate; Alcohols; Vinyl and allyl alcohols; Aldehydes; Acids, Preparation, Properties and structure; Acrylic, crotonic, and oleic acids.
Derivatives of Acetylene Series.................. 42
Propargyl alcohol; Propiolic acid; Linoleic acid.
General Discussion of Unsaturated Hydrocarbons and Derivatives 43

ORGANIC CHEMISTRY, PART 3

(*Continued*)

Pages

Polysubstitution Products of Saturated Aliphatic Hydrocarbons 44–58
Disubstitution Products and Derivatives 44–50
Dihalogen Compounds 44
Dihydroxy Alcohols or Glycols 45
Dialdehydes 49
Diketones 50
Trisubstitution Products and Derivatives 51–55
Trihydroxy Alcohols 51–53
  Composition and structure; Glycerol.
Esters of Glycerol 54–55
  Halohydrins; Nitroglycerine.
Polyhydroxy Alcohols 56–58
  Erythrol; Arabitol, and Xylitol; Mannitol; Dulcitol; Sorbitol.

ORGANIC CHEMISTRY, PART 4

Derivatives of Aliphatic Hydrocarbons—(*Continued*) 1–49
Monohydroxy Monobasic Acids 1– 9
  Composition and preparation; Hydroxy propionic acids; Hydroxy formic acid; Carbonic acid; Ethyl chlorcarbonate; Hydroxy acetic acid.
Hydroxy Propionic Acids 4– 8
  Isomerism; Stereoisomerism; Inactive lactic acid; Dextrolatic and levolactic acids; Hydracrylic acid.
Effects of Heat on Monohydroxy Monobasic Acids 8– 9
Saturated Dibasic Acids 10–19
  Physical properties; Oxalic acid; Malonic acid; Malonic-ester synthesis; Methyl malonic acid; Succinic acid; Pyrotartaric acid.
Unsaturated Diabasic Acids 20–23
  Fumaric acid; Maleic acid; Itaconic, citraconic and mesaconic acids.
Monohydroxy Dibasic Acid 24–25
  Tartronic acid; Malic acids.
Dihydroxy Dibasic Acids 26–30
  Mesoxalic acid; Tartaric acids; Salts of tartaric acid; Racemic acid; Mesotartaric acid; Levotartaric acid.

ORGANIC CHEMISTRY, PART 4
(*Continued*)

Pages

Monohydroxy Tribasic Acids 31–32
Citric acid; Salts of citric acid.

Carbohydrates 33–49
Classification and Nomenclature 33
Monosaccharoses 34–37
Aldehyde and Keto Alcohols 34
Bioses, Trioses, and Tetroses 35
Glycolic aldehyde; Glycerose; Erythrose.

Pentoses 36
Arabinose; Xylose; Rhamnose.

Hexoses 37
Glucose; Levulose; Galactose.

Disaccharoses 38–40
Sucrose; Cane sugar; Lactose; Maltose.

Trisoccharoses 41
Polysaccharoses 42–49
Starch; Cellulose; Manufacture of wood pulp; Amyloid and vegetable parchment; Mercerizing; Artificial silk; Nitrocelluloses; Guncotton; Celluloid; Dextrin; Glycogen; Inulin.

Glucosides 50–51
Amygdalin; Aesculin; Salicin; Populin; Phloridzin; Coniferin.

Mixed Compounds Containing Nitrogen 52–67
Amino Acids 52–54
Structure; Properties; Preparation; Amino acetic acid; Methyl amino acetic acid; Leucine; Asparagine.

Acid Amides 55–57
Preparation; Acetamide; Cyanamide; Guanidine; General properties; Acid amides of fatty-acid series.

Acid Imides 58
Urea and Derivatives 58–59
Uric Acid 60
Proteins 62–67
Composition, structure, properties, albumin; Globulin and fibrin; Peptones; Hemogloblin; Hematin; Casein; Gelatine; Tests.

ORGANIC CHEMISTY, PART 5

Pages

Aromatic or Benzene Series of Hydrocarbons.......... 1–21
Sources of Aromatic Hydrocarbons.................. 1– 3
Important Members of Aromatic Series.............. 4–21
  Benzine; Kekulé formula; Armstrong-Baeyer centric formula.
Nomenclature of Benzene Derivatives.............. 12–13
Orientation 14
Homologues of Benzene.......................... 15
  Toluene; Xylenes; Ethyl benzene; Trimethyl benzenes; Mesitylene; Cymene; Hexahydrobenzines, or Naphthenes.
Derivatives of Benzene Series.................... 22–61
Halogen Derivatives of Benzene and Its Homologues.. 23–31
  Addition products; Substitution products; Brombenzenes; Chlorine derivatives of benzene; Halogen derivatives of toluene.
Sulphuric and Sulphurous Acid Derivatives.......... 32–34
  Sulphonic acids; Sulphinic acids.
Nitric and Nitrous Acid Derivatives................ 35–38
  Nitro compounds; Nitro benzene; Nitrotoluenes; Nitroso compounds.
Amino Derivatives 39–42
  Preparation; Properties; Aniline; Aminotoluenes.
Derivatives of Aromatic Amines................... 43–48
  Anilides; Preparation and properties; Acetanilide; Alkyl and aryl amines; Monomethylaniline; Dimethylaniline; Diphenylamine; Triphenylamine.
Substituted Anilines 48
Diazo Compounds and Their Derivatives............ 49–53
  Diazotization; General laboratory method; Properties, structures, and reactions of diazo compounds.
Azo Compounds and Their Derivatives.............. 54–61
Azo Compounds 54–55
  Structure and formation; Phenylhydroxylamine; Azoxybenzene; Azobenzene; Hydrazobenzene.
Aminoazo Compounds 56–59
  Preparation; Aminoazobenzene; Acid yellow or fast yellow G; Fast yellow R; Butter yellow; Methyl orange; Diaminoazobenzene; Triaminoazobenzene; Bismarck brown.
Hydrazines 60–61

ORGANIC CHEMISTRY, PART 6

Pages

Derivatives of the Benzene Series.................. 1–43

Hydroxyl Derivatives 1–10

Phenols; Preparation; Properties; Reactions; Monohydroxy phenols; Phenol; Cresols; Thymol and carvacrol; Dihydroxy phenols; Catechol; Resorcinol; Quinol; Orcinol; Lithmus; Trihydroxy phenols; Pyrogallol; Phloroglucinol.

Derivatives of Phenols........................... 11–15

Ethers 11

Phenyl methyl and phenyl ethyl ethers; Guaiacol.

Substituted Phenols 11–16

Halogen phenols; Phenolsulphonic acids; Nitrosophenol; Mononitrophenols; Trinitrophenol; Aminophenols.

Alcohols 16

Preparation and properties; Benzyl alcohol.

Aldehydes 17–20

Preparation and properties; Benzaldehyde; Higher aromatic aldehydes; Cinnamic, cuminic, Anisic, and salicylic aldehyde; Vanillin; Piperonal.

Benzaldoximes 21

Ketones 22–23

Acetophenone; Benzophenone; Tetramethyldiaminobenzophenone.

Quinones 24

Acids 25–43

Monobasic Acids and Derivatives.................. 25–28

Benzoic acid; Benzoyl chloride; Benzoic anhydride; Toluic acids; Mesitylenic acid; Phenyl acetic acid; Hydrocinnamic acid.

Unsaturated Monobasic Acids...................... 29–30

Cinnamic acid; Phenyl propiolic acid; Ortho-nitrophenyl propiolic acid.

Dibasic Acids and Derivatives.................... 31–32

Phthalic acids; Phthalic anhydride and phthalimide; Phthalyl chloride; Isophthalic and terephthalic acids.

Nitro and Amino Acids and Derivatives............ 33–34

Nitrobenzoic acids; Anthranilic acid; Isatin; Hippuric acid.

Sulpho Acids and Derivatives..................... 35–38

Sulphobenzoic acids; Saccharin.

ORGANIC CHEMISTRY, PART 6
(Continued)

Pages

Monohydroxy Acids and Derivatives 39–40
Methods of formation; Salicylic acid.

Dihydroxy and Trihydroxy Acids 41–43
Protocatechuic acid; Gallic acid; Tannic acids; Leather; Inks.

Polynuclear Hydrocarbons and Derivatives 44–55
Preparation and properties; Diphenyl; Benzidine; Congo red; Diphenyl methane; Auramine; Mordants; Triphenylmethane.

Triphenylmethane Dyes 49–52
Color and structure; Malachite green; Pararosaniline; Rosaniline.

Phthalein Dyes 53–54
Phthalophenone; Phenolphthalein; Fluorescein; Eosin.

Dibenzyl and Derivatives 55
Stilbene.

ORGANIC CHEMISTRY, PART 7

Condensed-Ring Hydrocarbons 1–19
Naphthalene and Its Derivatives 1–13
Naphthalene; Homologues of naphthalene; Halogen naphthalenes; Nitronaphthalenes; Naphthaquinones.

Anthracene and Its Derivatives 13–20
Anthracene; Anthraquinone; Alizarin; Pupurin; Phenanthrene.

Terpenes 20–26
Source, general properties, and classifications; Hemiterpenes; True terpenes; Limonene; Phellandrene; Sylvestrene and thujene; Terpinene and teripnolene; Pinene; Bornylene and fenchene; Sesquiterpenes; Polyterpenes.

Oxidation Products of Terpenes 27–32
Unsaturated terpene alcohols; Geraniol; Linalol; Citronellol; Cyclic terpene alcohols; Borneol; Terpineol and pulegol; Menthol; Terpene aldehydes; Citral; Citronellal; Terpene ketones; Menthone; Camphor; Pulegone, fenchone, and thujone; Carvone; Phenols and phenolic ethers; Eugenol and safrol.

Cyclic Compounds 33–50
Alicyclic Compounds 34
Cyclopropane; Homologues of cyclopropane.

ORGANIC CHEMISTRY, PART 7

(*Continued*)

Pages

Heterocyclic Compounds 36

Five-membered rings; Furfuran; Furfural; Furfuryl alcohol, and pyromucic acid; Thiophen; Pyrrole; Pyrazole, pyrazoline, and pyrazolone; Antipyrine; Six-membered rings; Pyridine; Homologues of pyridine; Piperidine; Condensed heterocyclic compounds; Indole; Skatole; Quinoline.

Indigo 43–50

Natural indigo; Synthetic indigo; Vat dyes.

ORGANIC CHEMISTRY
(PART 1)

ALIPHATIC SERIES OF HYDROCARBONS

SATURATED HYDROCARBONS AND DERIVATIVES

INTRODUCTION

1. Beginning of Organic Chemistry.—Originally, general chemistry was divided into organic and inorganic chemistry, depending on whether or not substances were the product of some vital organized force. Even as late as the beginning of the 17th century, it was thought that organic compounds could be formed only under the influence of the life process. Unsuccessful attempts to form these compounds artificially served only to strengthen this belief. In 1828, however, Wöhler, a German chemist, prepared an organic compound, called *urea*, by simply allowing a water solution of ammonium cyanate, which is regarded as an inorganic compound, to evaporate. In 1856 Berthelot prepared acetylene by passing electric sparks between carbon poles in the presence of hydrogen.

Through these discoveries and the work of eminent French and German chemists, the prevalent idea of organic chemistry underwent a decided change. It is now realized that organic compounds are simply chemical compounds subject to the same governing laws as are inorganic chemical compounds, and are not dependent on the life process for their formation.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

Organic chemistry is simply the chemistry of the carbon compounds. A practical distinction between organic and inorganic bodies is their behavior when heated; an organic body is either converted into a vapor or is decomposed into volatile products, usually leaving a residue of carbon that burns away when heated in air.

2. **Sources of Compounds.**—Although the synthesis, or the artificial preparation of organic compounds, has caused the theory of the necessity of a vital force or life process for their formation to be rejected, the laboratory methods used for the preparation of these compounds are seldom the same as those employed by nature. In the laboratory it is usual to start with a few compounds that are formed by natural processes. Petroleum and coal form the basis for the production of the greatest number of organic compounds. Other organic compounds are made from the alkaloids, sugars, starch, etc.

3. **Classification of Compounds.**—The numerous organic compounds are divided into two main divisions, namely: the aliphatic, or fatty, compounds; and the aromatic compounds. These derive their names from the fact that the first division contains the animal and vegetable fats, and the second, to the fact that the earliest discovered compounds of this division possessed an agreeable aroma. The aliphatic compounds are considered as being derived from methane, CH_4; the aromatic compounds from benzene, C_6H_6.

PARAFFINS OR HYDROCARBONS OF THE METHANE SERIES

4. The saturated hydrocarbons (compounds of hydrogen and carbon), of the paraffin or methane series are remarkably stable; that is, they do not readily react with other substances, and because of this common property, they have been called the *paraffins*, from the Latin *parum* meaning *too little* and *affinis* meaning *akin*.

METHANE OR MARSH GAS, CH_4

5. Occurrence.—The simplest member of the paraffin series is methane, CH_4. It occurs in nature in the gases from volcanoes and is the principal constituent of so-called natural gas, samples of which having been found to contain from 37.5 to 99.2 per cent of CH_4. It is also found rising from marshes and from stagnant pools of water, for which reason it has been given the name *marsh gas*.

6. Synthesis From Elements.—Hydrogen and carbon do not react with each other at ordinary temperatures, but when a mixture of the two elements is heated to 1,200° C., methane is formed. Thus,

$$C+2H_2=CH_4$$

7. Berthelot's Synthesis.—Methane is prepared synthetically by passing a mixture of hydrogen sulphide and carbon disulphide over red-hot copper turnings.

$$2H_2S+CS_2+4Cu=4CuS+CH_4$$

8. Sabatier and Senderen's Synthesis.—When a mixture of carbon monoxide and hydrogen is passed over finely divided, reduced nickel heated to 275° C., methane is formed.

$$CO+3H_2=CH_4+H_2O$$

9. Other Methods.—When fairly pure methane is desired, it may be prepared in the laboratory by heating a mixture of anhydrous (dry) sodium acetate or potassium acetate with an alkali such as sodium hydroxide or calcium hydroxide. The reaction that takes place with sodium hydroxide is represented by the equation

$$NaC_2H_3O_2+NaOH=CH_4+Na_2CO_3$$

In practice a mixture of sodium hydroxide and calcium hydroxide that has been ignited is used. This mixture is called *soda lime*. Methane can also be prepared by treating aluminum carbide with water. The reaction is represented by the equation

$$C_3Al_4+12H_2O=3CH_4+4Al(OH)_3$$

10. Properties.—Pure methane is a colorless, odorless gas having a specific gravity of .559. It is soluble to the extent of 5.5 cubic centimeters in 100 cubic centimeters of water at 0° C., and in alcohol to the extent of 52 cubic centimeters in 100 cubic centimeters. The critical temperature of methane is −82.85° C., the critical pressure, 45.6 atmospheres. Solid methane melts at −184° C., forming a liquid that boils at −160° C., at atmospheric pressure. Methane burns quietly with a pale-blue flame. When it is mixed with air in the proportion of 1 volume to 10 volumes of air, an explosive mixture is formed that is easily ignited by spark or candle flame. This mixture is the cause of mine explosions and is known as *fire damp*. After an explosion of fire damp in a mine, there is always a quantity of carbon dioxide present, the carbon and hydrogen of methane uniting with the oxygen of the air according to the equation

$$CH_4+2O_2=CO_2+2H_2O$$

When methane is subjected to the action of electric sparks, it decomposes into carbon and hydrogen.

The chemical properties of methane are characteristic of the saturated hydrocarbons of the paraffin series. Such powerful oxidizing agents as nitric and chromic acids have practically no action on it, and sulphuric acid and alkalies do not attack it at all.

11. Composition.—In the preceding pages the chemical formula for methane has been given as CH_4. When a sample of methane is analyzed in the laboratory, it is found to consist of approximately 75 per cent. of carbon and 25 per cent. of hydrogen, and from these figures it is possible to calculate the empirical formula. Thus, dividing each percent. by the atomic weight,

$$75 \div 12.005 = 6.24$$
$$25 \div 1.008 = 24.80$$

Then, dividing each number so obtained by the smaller gives the number of atoms of each element in the compound.

$$6.24 \div 6.24 = 1 = \text{carbon}$$
$$24.80 \div 6.24 = 3.97 = \text{hydrogen}$$

In other words, methane consists of approximately 1 part of carbon and 4 parts of hydrogen. This fact suggests that the formula is CH_4 and that this is actually the case can be verified by other methods that will be taken up later.

12. Reactions of Methane and Halogens.—The stability of methane and the hydrocarbons of the paraffin series has already been referred to. However, these hydrocarbons react readily with chlorine and the other members of the halogen group and these simple reactions are very important since, once they are understood, similar reactions involving other members of the paraffin series are easily grasped. In this manner, by studying the properties and structure of a typical compound of any series, a knowledge of the subject of organic chemistry may be gradually and easily acquired.

13. When a burning jet of methane is brought into an atmosphere of chlorine, or when a mixture of methane and chlorine is ignited, the products of the reaction are always hydrochloric acid and carbon, which is additional proof of the composition of methane. The reaction that takes place between methane and chlorine is represented by the equation

$$CH_4+2Cl_2=4HCl+C$$

The above reaction takes place instantaneously and, under the conditions last mentioned, with explosive violence.

If, however, the reaction between methane and chlorine is caused to proceed slowly, as is the case when a mixture of the two gases contained in a glass vessel is exposed to diffused sunlight, four different chlorine compounds of methane will be formed. They are monochlormethane or methyl chloride, CH_3Cl, in which one hydrogen atom of methane has been replaced by chlorine, thus:

$$CH_4+Cl_2=CH_3Cl+HCl$$

Dichlormethane or methylene chloride, CH_2Cl_2, in which two hydrogen atoms of methane have been replaced by chlorine, thus:

$$CH_4+2Cl_2=CH_2Cl_2+2HCl$$

Trichlormethane or chloroform, $CHCl_3$ in which three hydrogen atoms of methane have been replaced by chlorine, thus:

$$CH_4+3Cl_2=CHCl_3+3HCl$$

Tetrachlormethane or carbon tetrachloride, CCl_4, in which the four hydrogen atoms of methane have been replaced by chlorine, thus:

$$CH_4+4Cl_2=CCl_4+4HCl$$

14. Substitution Products.—In the formation of the chlorine compounds of methane it is assumed that each hydrogen atom is replaced by chlorine in successive steps. Thus, in the formation of tetrachlormethane, CCl_4, mono-, di- and trichlormethane are first formed by the use of the method described. In other words, it is assumed that when one or more of the hydrogen atoms of methane is replaced, the remaining hydrogen atoms of the molecule are not disturbed. To reactions such as these the term *substitution* is applied and the products formed are known as *substitution products.*

In the examples given monovalent hydrogen has been replaced, atom for atom, by monovalent chlorine. It is also possible to replace, indirectly, two or three atoms of hydrogen in methane by divalent and trivalent elements or groups of elements acting with valences of one, two, or three, as will be shown subsequently.

The fact that one, two, three, or four atoms of chlorine acting on methane replace an equal number of hydrogen atoms does not prove that the chlorine occupies the same place the hydrogen did, although a careful study of the facts regarding the products formed in this way leads to the belief that the substituting atom, or group, does occupy the same place, or does bear the same relation to the carbon atom as did the replaced hydrogen atom.

15. Valence of Carbon.—In all that has gone before, the tetravalency of the carbon atom has been assumed. That this assumption is absolutely correct is not capable of direct proof, although the majority of facts indicate that in all but a few compounds the valence of carbon is always four.

16. Saturated and Unsaturated Compounds.—In methane one carbon atom is directly connected to four monovalent hydrogen atoms, which indicates that the valence of carbon is four. Again, it has been shown that when methane reacts with chlorine it does so only at the expense of its hydrogen atoms. In other words, chlorine cannot be added to the molecule and a hypothetical compound with the formula CH_4Cl formed. This fact indicates that the carbon atom in methane has all of its four valences satisfied by the four hydrogen atoms. The carbon atom in methane is, therefore, saturated and a saturated compound may be defined as one in which all of the valences of the carbon atoms that it contains are satisfied. Saturated compounds of the aliphatic series can only form substitution products with other elements or groups of elements.

17. Opposed to the saturated type of compound there is the unsaturated type of compound of the aliphatic series. The simplest unsaturated compound of this series is one having the formula C_2H_4. It is obvious that if in methane, CH_4, the four valences of carbon are satisfied, then in the compound C_2H_4 there are only one-half enough hydrogen atoms for saturation, if the valence of carbon is four. Since experimental evidence leads us to believe that the valence of carbon is four in this compound, the valences of the carbon atoms in it must be unsatisfied. Therefore, C_2H_4, or *ethylene*, as it is called, is an example of an unsaturated compound, which may be simply defined as a compound in which all of the valences of its carbon atoms are not satisfied.

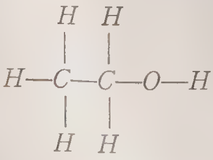
18. Structural and Graphic Formulas.—The analysis of an organic substance gives its composition from which is derived its empirical and molecular formulas. In organic chemistry, however, there are compounds that have the same percentage composition and the same molecular formula, but which possess different properties; so it becomes necessary to provide a formula to show the difference between these compounds. This is accomplished by supposing the atoms of the compound to be linked together by bonds in such a manner that this linking can be represented by a structural formula, which may be defined as the formula that denotes the mode of arrangement of the atoms of a molecule.

Structural formulas are based on the fact that carbon cannot combine with more than four similar or dissimilar monovalent atoms or atomic groups, and that no difference can be discovered in the four affinities of carbon when they form compounds. The formulas also depend on the fact that carbon atoms can unite with each other and can be linked together in single, double, or triple union, as will be shown subsequently. Formulas are also written with lines or dashes connecting the atoms of the compound, in which form they are called graphic formulas.

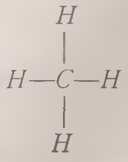
Table I will make clear the differences in empirical, structural, and graphic formulas:

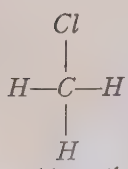
TABLE I

TYPES OF FORMULAS

Compound	Formula	Remarks
Ethyl alcohol	Empirical C_2H_6O	Shows composition only
	Structural C_2H_5OH	Shows that it contains an ethyl (C_2H_5) group and a hydroxyl group
	Graphic  $H-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-\overset{\overset{H}{\vert}}{\underset{\underset{H}{\vert}}{C}}-O-H$	Shows the valence of each atom as well as the structure of the molecule

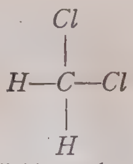
19. Structure of Methane.—Because of the experimental evidence that exists, it is believed that methane is a saturated compound and that when it reacts with chlorine, the latter replaces a hydrogen atom and takes its place in the methane molecule. Further knowledge concerning the structure of the methane molecule is gained when the question of the relation of each hydrogen atom to the carbon atom is considered. In the first place, no matter what the methods used for their preparation, the four chlorine compounds of methane always correspond to the formulas CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Thus, there is only one known compound having the properties and formula of monochlormethane. This condition can exist only if the hydrogen atoms of methane are of equal value. This may still further explained by numbering the hydrogen atoms of methane as follows: $C-\underset{1}{H}-\underset{2}{H}-\underset{3}{H}-\underset{4}{H}$. Now if each hydrogen atom of methane bears a different relation to the carbon atom than the others then four totally different monochlormethanes might be expected. Thus, depending upon which hydrogen atom was replaced first, it would be possible to obtain, $C-Cl-\underset{2}{H}-\underset{3}{H}-\underset{4}{H}$; $C-\underset{1}{H}-Cl-\underset{3}{H}-\underset{4}{H}$; $C-\underset{1}{H}-\underset{2}{H}-Cl-\underset{4}{H}$ and $C-\underset{1}{H}-\underset{2}{H}-\underset{3}{H}-Cl$. But since only one monochlormethane is known, it can only be believed that all of the hydrogen atoms of methane are of equal value and that their relations to the carbon atom are the same. For these reasons methane and similar molecules are called symmetrical.

20. In order to represent the facts that methane is a saturated compound and that the hydrogen atoms that it contains are grouped about the carbon atom in a symmetrical manner, the graphic formula  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$ is used. This formula also shows that carbon is tetravalent, each line drawn from the carbon atom indicating a bond of valence, and likewise that hydrogen is monovalent, since each atom is connected to carbon by only one line. The graphic formulas for the four chlorine compounds of methane may now be written. They are as follows:



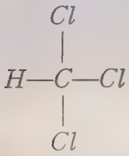
$$\begin{array}{c} Cl \\ | \\ H-C-H \\ | \\ H \end{array}$$

monochlormethane



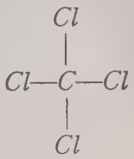
$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ H \end{array}$$

dichlormethane



$$\begin{array}{c} Cl \\ | \\ H-C-Cl \\ | \\ Cl \end{array}$$

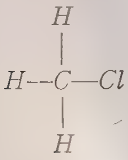
trichlormethane



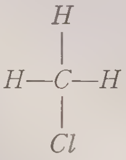
$$\begin{array}{c} Cl \\ | \\ Cl-C-Cl \\ | \\ Cl \end{array}$$

tetrachlormethane

It should, of course, be realized that, since the hydrogen atoms of methane are of equal value, any one of them may be replaced by chlorine. Thus, the formula for monochlormethane is also correctly written

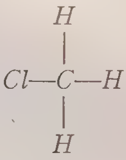


$$\begin{array}{c} H \\ | \\ H-C-Cl \\ | \\ H \end{array}$$



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ Cl \end{array}$$

or



$$\begin{array}{c} H \\ | \\ Cl-C-H \\ | \\ H \end{array}$$

The same applies to dichlormethane and trichlormethane.

21. Radicals.—When chlorine reacts with methane to form monochlormethane,

$$CH_4+Cl_2=CH_3Cl+HCl$$

it is assumed that the chlorine first removes one atom of hydrogen from the methane molecule and forms hydrochloric acid. The remaining chlorine atom then unites with the unsaturated residue CH_3 to form CH_3Cl. This unsaturated residue CH_3 is known as a radical, just as are SO_4 and OH in inorganic chemistry. The radical CH_3 is monovalent because only one of the four valences of carbon is left unsatisfied. In a similar manner the radical CH_2 is divalent, since two of the valences of carbon are unsatisfied. The radical CH_3 has been given the name *methyl*, and compounds containing it are called *methyl compounds*. Thus, monochlormethane may also be called methyl chloride, while as a group the monohalogen compounds of methane are called *methyl halides.* As progress is made in the study of organic chemistry, it will be seen that a large number of groups of elements take part in reactions in a manner similar to that of the methyl group.

The general name that has been given to the radicals of saturated hydrocarbons is *alkyl.* Thus, an alkyl halide is a compound of a halogen atom and a radical of the paraffin series. Methyl chloride contains the alkyl radical methyl, and the halogen atom chlorine. It is, therefore, an alkyl halide. Sometimes equations for general reactions are written in which the alkyl radical is represented by R and the halogen atom by X. Thus, RX represents an alkyl halide.

HALOGEN COMPOUNDS OF METHANE

22. Methyl Chloride, CH_3Cl.—As previously stated, methyl chloride is formed when a mixture of methane and chlorine is exposed to the action of diffused sunlight. The other chlorine substitution products of methane are also formed, however, and it is impossible so to regulate the reaction as to obtain pure methyl chloride. It is more easily prepared by treating methyl alcohol or wood alcohol, with hydrochloric acid gas according to the reaction

$$CH_3OH + HCl = CH_3Cl + H_2O$$

23. Methyl chloride is also prepared by heating a mixture of one part of methyl alcohol, two parts of common salt, and three parts of concentrated sulphuric acid. Pure methyl chloride, at ordinary temperatures, is a colorless gas having a peculiar, agreeable odor and a sweet taste. About 400 parts by volume are soluble in 100 parts of water and 3,500 parts in 100 parts of alcohol. The specific gravity of the gas is .9197 at 18° C. Methyl chloride is easily liquified, and the liquid boils at $-23.73°$ C.; it may be frozen to a solid that melts at $-91.5°$ C. Methyl chloride is inflammable, and, when ignited, burns with a greenish flame, which is characteristic of halogen compounds. Methyl chloride is used in the manufacture of coal-tar colors and to some extent as a refrigerating agent.

24. Reversible Reactions.—It will be noted that water is formed by the reaction between methyl alcohol and hydrochloric acid and when water comes in contact with methyl chloride the latter reacts to form the original alcohol and acid. Thus,

$$CH_3Cl+H_2O=CH_3OH+HCl$$

A reaction such as this is termed *reversible* and is usually written

$$CH_3OH+HCl\rightleftharpoons CH_3Cl+H_2O$$

Reversible reactions are commonly met with in organic chemistry. In the present case, when a certain combination of methyl chloride and water is formed, the reaction stops because a condition of equilibrium is reached between methyl alcohol, hydrochloric acid, methyl chloride, and water. After equilibrium is reached, however, most organic reactions may be made to proceed further, but seldom to completion, by varying the conditions of the reaction. Thus, if one or more of the reaction products are removed as fast as formed, the reaction may be made to proceed much further. In the case of methyl chloride the reaction with water is greatly lessened by the presence in solution of concentrated sulphuric acid or zinc chloride, which act as dehydrating agents.

25. Methyl Bromide, CH_3Br, and Methyl Iodide, CH_3I. Methyl bromide is formed when methane and bromine are brought together in the presence of diffused sunlight. Methyl iodide, however, cannot be obtained in this way because of the reducing action of the hydriodic acid, which is set free. This converts the methyl iodide, as fast as it is formed, back into methane and iodine. Thus,

$$CH_4+I_2=CH_3I+HI$$
$$CH_3I+HI=CH_4+I_2$$

Methyl bromide and methyl iodide are usually prepared by the action of phosphorus and the halogens on methyl alcohol. It is supposed that phosphorus tribromide or phosphorus triiodide is first formed,

$$P_4+6Br_2=4PBr_3$$
$$P_4+6I_2=4PI_3$$

and that the phosphorus halide then reacts with methyl alcohol to form the monohalogen substitution product. Thus,

$$3CH_3OH+PBr_3=3CH_3Br+H_3PO_3$$
$$3CH_3OH+PI_3=3CH_3I+H_3PO_3$$

These halogen derivatives are also formed by the action of hydrobromic and hydriodic acids upon methyl alcohol in the same manner as is methyl chloride.

26. Methyl bromide is a colorless, transparent liquid. with a burning taste and an odor resembling that of chloroform. It has a specific gravity of 1.732 at 0° C.; and boils at 4.5° C. It burns feebly and is only slightly soluble in water, but it is soluble in alcohol. Methyl iodide is a colorless, transparent liquid that turns brown on exposure to light. Its specific gravity at 15° C. is 2.2852. It has a pleasant ethereal odor, boils at 42.35° C.; is insoluble in water, but is soluble in alcohol. It is used in the manufacture of dyes.

27. Methylene Iodide, CH_2I_2.—Methylene iodide, the principal halogen derivative of methane containing two halogen atoms, is prepared by the reduction of iodoform by hydriodic acid in a sealed tube, when the reaction is

$$CHI_3+HI=CH_2I_2+I_2$$

At 0° C. it solidifies in the form of leaflets, but at ordinary temperatures is a yellow liquid remarkable for its high specific gravity, which is 3.33 at 15° C. It is the heaviest organic liquid known, boils at 180° C., and is soluble in alcohol and ether. It is used for determining the specific gravities of precious stones and for separating mixtures of minerals.

28. Methylene Chloride, CH_2Cl_2.—Methylene chloride is prepared by treating a mixture of methyl alcohol and chloroform with nascent hydrogen. This halogen derivative is a colorless liquid, has a specific gravity of 1.2615 at 17° C., boils at 41.6° C., and is soluble in alcohol and ether, but is insoluble in water. It is used as a spray to produce local anesthesia.

29. Methylene Bromide, CH_2Br_2.—Methylene bromide is prepared in a similar manner as the corresponding chloride, by the reduction of an alcoholic solution of bromoform. It is a colorless or slightly yellow liquid, insoluble in water, but is soluble in alcohol and ether. It boils at 98.5° C. and has a specific gravity of 2.498 at 15° C.

30. Chloroform, $CHCl_3$.—Chloroform, or trichlormethane, the trihalogen derivative of methane and chlorine, was discovered simultaneously in 1851 by Liebig and Soubeiran. It may be prepared by distilling dilute alcohol or acetone with bleaching powder, or by reducing carbon tetrachloride with nascent hydrogen. On a large scale, a mixture of acetone* and bleaching powder is heated to 65° C. In the reaction that takes place, trichloracetone, $CH_3CO{\cdot}CCl_3$, is probably first formed. Thus,

$$CH_3CO{\cdot}CH_3+3Cl_2=CH_3CO{\cdot}CCl_3+3HCl$$
$$2CH_3CO{\cdot}CCl_3+Ca(OH)_2=2CHCl_3+Ca(CH_3COO)_2$$

With alcohol the reaction goes as follows: The alcohol is first oxidized to acetaldehyde,

$$C_2H_5OH+Cl_2=CH_3COH+2HCl$$

and the acet aldehyde is then transformed into the trichloraldehyde, or chloral, thus:

$$CH_3{\cdot}COH+3Cl_2=CCl_3{\cdot}COH+3HCl$$

This substance, when treated with a base, which in this instance is the slaked lime present in the bleaching powder, breaks down, forming chloroform and calcium formate, thus:

$$2CCl_3{\cdot}COH+Ca(OH)_2=2CHCl_3+Ca(COOH)_2$$

The distillate obtained by the use of acetone or alcohol consists of water and chloroform, which separate into two layers. The lower layer of chloroform is then drawn off, washed with clean water, separated from it, and agitated with concentrated sulphuric acid in order to remove the last traces of water. When the chloroform has again separated from the sulphuric acid, this time being the upper layer, it is drawn off and purified by distillation.

---

*When describing the preparation of organic compounds, it is frequently necessary to mention the names of compounds not previously treated. These compounds will, however, be taken up in their proper places.

31. Laboratory Preparation of Chloroform.—From 400 to 500 grams of bleaching powder are made into a cream with water. The cream is then placed in a round-bottom, two-liter flask *a*, Fig. 1, which is connected with a condenser *b*. About 100 cubic centimeters of acetone or alcohol is slowly added through the dropping funnel *c* that passes through the tight cork inserted in the neck of the flask. The contents of the flask may now be gently heated either over a water bath *d* or a sand bath, the first being preferable. A vigorous reaction takes place and a mixture of acetone or alcohol, water, and chloroform distils over. The chloroform usually collects as a heavy oil at the bottom of the receiver *e*, but, if sufficient alcohol or acetone is present with it, a solution is formed that is soluble in the water gathered in the receiver. Thus, if two liquid layers are not visible in the receiver, a large quantity of water added to its contents will precipitate the chloroform. The latter is then separated from the water layer by means of a separatory funnel, similar to *c*, shaken with sulphuric acid to remove water and alcohol, and the chloroform is then redistilled over a water bath.

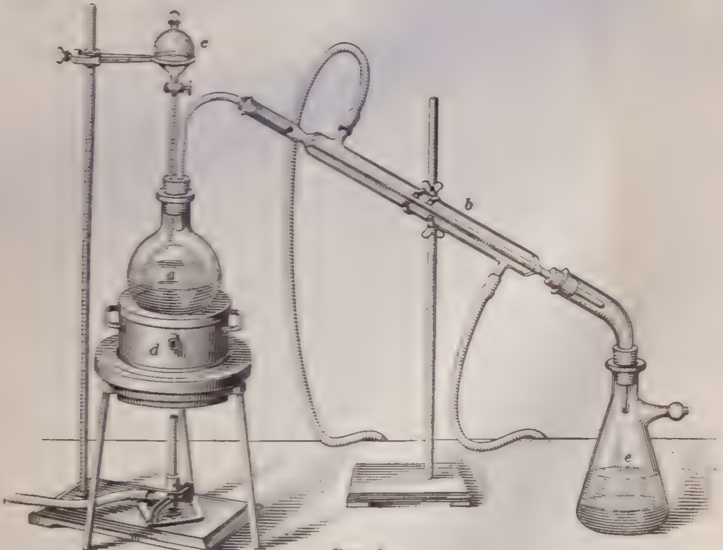


Fig. 1

32. Properties of Chloroform.—Chloroform is a thin, colorless, very mobile, non-inflammable liquid, with a characteristic, agreeable, ethereal odor, and sweetish taste. It is highly refractive, has a specific gravity of 1.498 at 15° C., and boils at 61° C. It is only slightly soluble in water, but is readily soluble in alcohol, ether, and benzene. It is used as a solvent for sulphur, phosphorus, fats, resins, and a number of the alkaloids. It is also extensively used in surgery as an anesthetic, prolonged inhalation causing unconsciousness. Chloroform is a rather unstable compound, being decomposed by air and light into chlorine, hydrochloric acid, phosgene, or carbonyl chloride, $COCl_2$, and carbon dioxide:

$$4CHCl_3+3O_2=2COCl_2+4HCl+2Cl_2+2CO_2$$

This decomposition is especially noticeable in very pure samples of chloroform, and it is prevented by the addition of an impurity, usually alcohol, added to the extent of 1 per cent.

When chloroform is heated with an alcoholic solution of potash and aniline, phenyl carbylamine or phenyl isocyanide is formed. As this has a very strong characteristic odor, it forms a delicate and easily recognizable test for chloroform and aniline and is called the *carbylamine reaction*.

$$CHCl_3+3KOH+C_6H_5NH_2=C_6H_5NC+3KCl+3H_2O$$

The carbylamine reaction should be carried out under a hood, a test tube and one drop of aniline, two drops of chloroform, and one cubic centimeter of alcoholic potash being used. After making the test the contents of the test tube should be carefully discarded into a drain pipe. Burns caused by phenyl isocyanide are very painful.

When chloroform is heated to 180° C. in a sealed tube with alcoholic ammonia, (NH_3 in alcohol) the three atoms of chlorine are replaced by nitrogen, with the formation of ammonium cyanide, NH_4CN. This reaction is

$$CHCl_3+5NH_3=3NH_4Cl+NH_4CN$$

When heated with sodium ethoxide, $NaOC_2H_5$, the halogen atoms of chloroform take part in a double decomposition, yielding orthoformic ether, as is shown by the equation

$$CHCl_3+3NaOC_2H_5=3NaCl+CH(OC_2H_5)_3$$

33. Iodoform, CHI_3.—The halogen derivative iodoform holds a very important position in surgery. It was discovered in 1822 by Serullas. It is formed from a number of substances such as alcohol, acetone, or an aldehyde, by the action of iodine and an alkaline hydroxide. Acetone is generally used in the manufacture of iodoform, being less expensive than alcohol. Iodoform is easily prepared in the laboratory by dissolving 2 grams of sodium carbonate in 10 grams of water, adding 1 gram of alcohol, and heating the solution to 80° C., then gradually adding 1 gram of iodine when the iodoform separates in yellow scales. Iodoform is also prepared by the electrolysis of a solution of potassium iodide, sodium carbonate, and alcohol.

Iodoform is a solid, crystallizing in small, lustrous scales, or as a crystalline powder. It has a strong, peculiar, saffron-like odor, is insoluble in water, but is soluble in alcohol and ether. It sublimes readily, melts at 119° C., and has a specific gravity of 4.08. It is used in surgery as an antiseptic and disinfectant. It has, in itself, no direct action upon bacteria, its action depending on its decomposition resulting from the warmth of the body and the secretions of the wound.

The production of iodoform is a very delicate test for alcohol, although acetone, aldehyde, and any other substances containing the group $CH_3—C$, in union with oxygen, yield iodoform. This test is carried out by adding iodine to the liquid to be tested, then adding caustic potash drop by drop until the color of the iodine is destroyed. If considerable alcohol is present a yellow precipitate forms at once, while if only traces are present the precipitate forms rather slowly.

34. Bromoform, $CHBr_3$.—The methods of obtaining bromoform are similar to those used to obtain chloroform. It is usually prepared by either of the following methods: Potassium hydroxide is dissolved in its own weight of dilute alcohol or acetone, and the solution thoroughly cooled. Bromine is then added in small quantities until the color of the liquid becomes permanent. The product is shaken with water, when the bromoform separates in the form of an oily liquid, which is washed, dried, and rectified. The other method is to treat calcium hypobromite with alcohol or acetone.

Bromoform is a colorless, oily liquid that has a specific gravity of 2.8887 at 10° C. and has an odor and taste like that of chloroform. It is soluble in alcohol and ether, but is almost insoluble in water. It melts at 9° C. and boils at 151.2° C. It is used largely in medicine.

35. Carbon Tetrachloride, CCl_4.—Carbon tetrachloride is formed whenever chloroform or carbon disulphide is acted upon by chlorine. The reactions are

$$CHCl_3+Cl_2=CCl_4+HCl$$
$$CS_2+3Cl_2=CCl_4+S_2Cl_2$$

Carbon tetrachloride is a heavy, colorless, non-inflammable liquid that has an agreeable aromatic odor and a specific gravity of 1.5835 at 25° C.; it is insoluble in water, but is soluble in alcohol and ether. It boils at 76.74° C. and when heated with an excess of water to 250° C., it decomposes, forming hydrochloric acid and carbon dioxide. It is used as a solvent in the fat and oil industries where its property of non-inflammability renders it particularly valuable. It is also used in fire extinguishers and in cleaning compounds.

ETHANE

36. Occurrence and Preparation.—Ethane, C_2H_6, is found dissolved in petroleum as the latter issues from the earth and mixed with methane, it is a constituent of natural gas. It is formed when ethyl chloride is treated with nascent hydrogen, as shown in the equation

$$C_2H_5Cl+2H=C_2H_6+HCl$$

It is also formed when zinc ethyl is treated with water, as is shown by the equation

$$Zn(C_2H_5)_2+H_2O=2C_2H_6+ZnO$$

Ethane can also be made by treating the iodine substitution product of methane, methyl iodide, CH_3I, with zinc or sodium in some neutral medium, preferably ether, according to the following reaction:

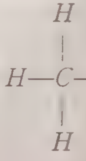
$$2CH_3I+2Na=C_2H_6+2NaI$$

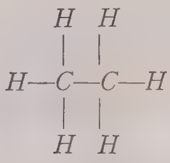
This last method for the formation of ethane is one that is used extensively in the building up of complex hydrocarbons from the more simpler ones.

Ethane is a colorless, odorless gas having a specific gravity of .446 at 0° C. Its critical temperature is 32.1° C. and its critical pressure 48.85 atmospheres. It boils at −84.1° C. under a pressure of 749 millimeters and solidifies at −172.1° C. Ethane closely resembles methane in most of its properties, it is not reacted upon by most reagents, and is about twice as soluble in alcohol. The action of chlorine upon ethane is exactly the same as its action upon methane.

37. Structure.—A chemical analysis of ethane shows it to have the composition represented by the formula C_2H_6. According to this formula, however, if carbon is tetravalent, only six of its valences have been satisfied by hydrogen, and ethane would appear to be an unsaturated compound. But ethane is known to be a saturated compound, since the only way in which it can react with the halogens is by losing hydrogen. As previously stated, ethane is formed when methyl iodide and sodium or zinc are brought together, in ethereal solution.

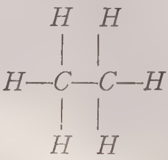
$$2CH_3I+2Na=C_2H_6+2NaI$$
$$2CH_3I+Zn=C_2H_6+ZnI_2$$

As in the replacement of hydrogen by chlorine in methane, which first forms the radical CH_3, which, in turn, combines with a second atom of chlorine to form CH_3Cl, the action of sodium on methyl iodide may be regarded as being analogous. In this reaction, however, the sodium does not replace the iodine. It merely removes it from methyl iodide, leaving the two radicals CH_3 and CH_3. Now, in each of these radicals, carbon has been left with one valence unsaturated. In other words, the radical has a valence of one and may be represented as CH_3, or graphically as  $H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-$ and when two such radicals are brought together, the result is $CH_3—CH_3$, or



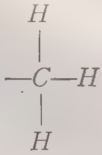
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

in which the valence of each radical satisfies the other. Thus, in the formula



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

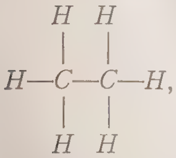
it may be considered that each CH_3, or



$$-\underset{H}{\overset{H}{C}}-H$$

group has taken the place of hydrogen in the methane molecule just as did chlorine in monochlormethane.

38. On account of its structure ethane may also be considered as dimethyl, because it consists of two methyl groups; or as methyl methane, since it is formed by substituting a methyl group for hydrogen in the methane molecule. The formula for ethane may be variously written as follows:



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H,$$

$$CH_3—CH_3, \qquad CH_3{\cdot}CH_3$$

or simply C_2H_6. It will be noted that the center period serves the same purpose as the dash.

What has been said concerning the structure and formula of methane is also true of ethane. Thus, the graphic formula of ethane shows each of its carbon atoms as having all of their four valences satisfied. The symmetry of the ethane molecule is also borne out by the fact that all of its hydrogen atoms are of equal value. Thus, no matter what the method used for its formation, only one monochlorethane is known. As in the case of methyl chloride, it is assumed that, in the formation of monochlorethane, hydrogen is first removed from the ethane molecule, leaving the residue C_2H_5, which then reacts with another atom of chlorine to form monochlorethane. The residue C_2H_5 is the radical of ethane, just as CH_3 is the radical of methane. It is known as *ethyl*.

39. The theory and facts concerning the tetravalency of the carbon atom and the structure of methane and ethane have been thoroughly treated, and what has been said concerning the preparation of these two compounds is also true of the other compounds of the paraffin series. The formulas for methane and ethane are CH_4 and C_2H_6, respectively, and attention is directed to the fact that the difference existing between these formulas is CH_2. About fifty hydrocarbons of

TABLE II

HYDROCARBONS OF PARAFFIN SERIES

Name of Compound	Formula	Physical State	Boiling Pt. Degrees C. 760 mm.	Specific Gravity
Methane	CH_4	Gas	−164.0	.41(−164°)
Ethane	C_2H_6	Gas	− 90.0	.446(0°)
Propane	C_3H_8	Gas	− 44.1	.515(16°)
Butane	C_4H_{10}	Gas	.3	.60(0°)
Pentane	C_5H_{12}	Liquid	36.4	.6337(15°)
Hexane	C_6H_{14}	Liquid	69.05	.6603(20°)
Heptane	C_7H_{16}	Liquid	98.4	.694(20°)
Octane	C_8H_{18}	Liquid	125.6	.7062(15°)
Nonane	C_9H_{20}	Liquid	150.5	.7219(15°)
Decane	$C_{10}H_{22}$	Liquid	173.0	.7454(0°)
Undecane	$C_{11}H_{24}$	Liquid	195.0	.7581(20°)
Dodecane	$C_{12}H_{26}$	Solid	214.5	.7684(20°)
to				
Hexacontane	$C_{60}H_{122}$	Solid		

the paraffin series are known, but, since most of them are of theoretical and not of practical importance, and their chemical behavior is practically the same as that of methane and ethane, only a few of the most important from a practical standpoint will be treated. A list of the hydrocarbons of the paraffin series is given in Table II. It will be noted that the formula of each compound differs from the one before and after it by CH_2.

40. Ethyl Chloride, C_2H_5Cl.—Ethyl chloride is prepared by the methods employed for the preparation of methyl chloride, except that ethane or ethyl alcohol is used instead of methane or methyl alcohol. The laboratory apparatus used is shown in Fig. 2. The process is carried out as follows: Hydrochloric-acid gas is generated in the flask *a* by dropping concentrated sulphuric acid from the funnel *b* on concentrated hydrochloric acid. The gas so generated passes through the

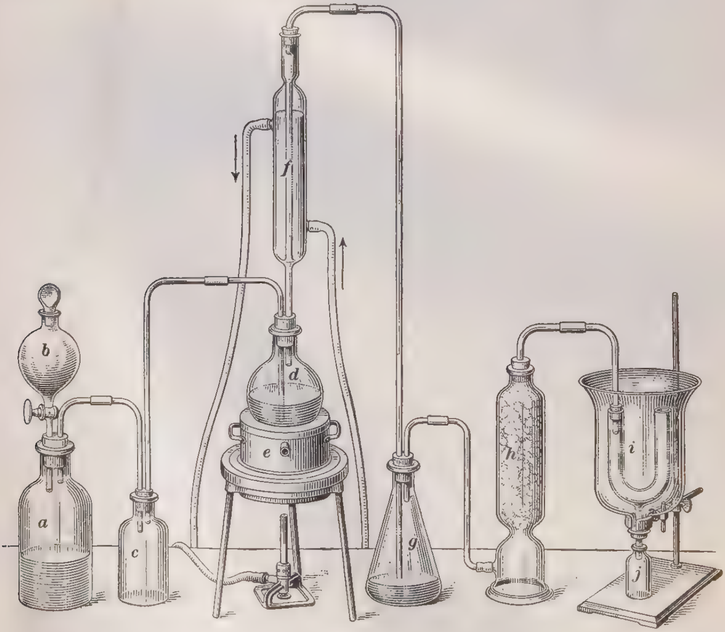


FIG. 2

safety bottle *c* and into a mixture of ethyl alcohol and zinc chloride contained in the flask *d*, which rests on the hot-water bath *e*. A reaction takes place between the hydrochloric-acid gas and the ethyl alcohol to form ethyl chloride,

$$C_2H_5OH+HCl=C_2H_5Cl+H_2O$$

The water formed is removed from the mixture by the zinc chloride. Alcohol vapors, excess hydrochloric-acid gas, and ethyl chloride pass up through the reflux condenser *f*, the alcohol being condensed and caused to drop back into the flask *d*, while the hydrochloric acid gas is for the most part absorbed by the water in the wash-bottle *g* and the remainder being retained by the mixture of calcium hydroxide and sodium hydroxide (soda lime) contained in the absorbing tower *h*. The ethyl chloride passes on into the condensing system *i* and which consists of a **U** tube immersed in a freezing mixture and is collected in the receiver *j*, which, during the experiment, is packed in ice.

41. Certain conditions, such as a sudden reduction in temperature of the generator *a*, Fig. 2, may cause the contents of the reaction flask *d* to be drawn back toward the generator *a*. If this should occur, using the apparatus described, no accident will result by reason of the contact of the alcohol with sulphuric acid, since the contents of the flask *d* will be trapped in the safety bottle *c*, which should be large enough to hold the entire contents of the reaction flask *d*.

At ordinary temperatures ethyl chloride is a gas, but below 12.2° C., its boiling point, it is an extremely volatile liquid having a penetrating, aromatic odor and a specific gravity of .9214 at 0° C. It is soluble in alcohol and somewhat soluble in water, and burns with a green flame.

42. Ethyl Bromide, C_2H_5Br.—Ethyl bromide is formed when ethyl alcohol is treated with phosphorus tribromide or phosphorus pentabromide at ordinary temperatures, or when alcohol is heated with hydrobromic acid.

It is prepared by dropping bromine by means of a funnel into a mixture of alcohol and amorphous phosphorus contained in a distilling flask that is immersed in cold water and connected to a condenser. After all of the bromine has been added, the mixture is allowed to stand for about an hour and is then distilled. The reaction that takes place in the formation of ethyl bromide by this method may be represented by the following equation:

$$12C_2H_5OH + P_4 + 6Br_2 = 12C_2H_5Br + 4H_3PO_3$$

43. Ethyl bromide is still more conveniently prepared by adding 1 part of ethyl alcohol in small portions and with constant shaking to 2 parts of concentrated sulphuric acid contained in a round-bottom flask. After the mixture has cooled down to room temperature, about 1 part of ice water is carefully added, the contents of the flask being simultaneously agitated and cooled. Finally, 1 part of powdered potassium bromide is added. The flask is now connected to a long condenser and heated over a sand bath, the temperature being such that the distillation proceeds at the rate of about 60 drops a minute.

The end of the condenser is fitted with an adapter, the end of which reaches very nearly to the bottom of the receiver. Just before the distillation is begun, about an inch of ice water is placed in the receiver, which is in turn placed in an ice water bath. All of these precautions are taken because of the low boiling point of ethyl bromide, which collects below the water layer in the receiver. This bottom layer is washed several times with cold water to remove the alcohol, and then with a dilute solution of sodium carbonate. A final separation from water is then made by use of a separatory funnel, and the ethyl bromide is dried by allowing it to stand in contact with anhydrous calcium chloride. When dry it is redistilled over a water bath heated to about 60° C.

44. The reactions that occur in the preparation of ethyl bromide by the foregoing method are represented by several equations. The reaction between ethyl alcohol and sulphuric acid yields ethyl sulphuric acid

$$C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$

The ethyl sulphuric acid then reacts with potassium bromide to form ethyl bromide and potassium bisulphate

$$C_2H_5HSO_4 + KBr = C_2H_5Br + KHSO_4$$

Ethyl bromide is a colorless, inflammable, volatile liquid that has a burning taste and a pleasant ethereal odor. Its specific gravity is 1.438 at 25° C., and its boiling point is 38.4° C. It is soluble in alcohol, ether, and chloroform, but is insoluble in water. It is used as a local anesthetic in minor surgery.

45. Ethyl Iodide, C_2H_5I.—Ethyl iodide is prepared by adding 10 parts of finely powdered iodine to a mixture of 1 part of red phosphorus and 8 parts of absolute (100 per cent.) alcohol contained in a flask with a round-bottom. The iodine is added gradually during a period of about 20 minutes, the flask being frequently shaken and cooled after each addition of iodine by immersion in ice water. When all of the iodine has been added, the flask is fitted with an air condenser, which consists of an ordinary glass tube about 6 millimeters (¼ inch) in diameter, held in a vertical position. The flask is now allowed to stand for at least 5 hours, or, better, overnight. To complete the reaction the air condenser is removed and replaced by a reflux condenser and then heated over a water bath for about 2 hours. After cooling, the flask is connected to the condenser in the regular way and the ethyl iodide distilled over a rapidly boiling water bath. The distillate, which is colored brown by iodine, is washed with several portions of water to remove the alcohol, and then with a dilute (.5 per cent.) solution of caustic soda, which removes the iodine. After finally separating the water by means of a separatory funnel, the ethyl iodide is dried by slowly pouring it over anhydrous calcium chloride held in a funnel. The product is now distilled, that portion coming over between 70° and 75° C. being collected.

Ethyl iodide is a clear, colorless liquid, with a pleasant odor. It has a specific gravity of 1.944 at 15° C., boils at 73° C., and is insoluble in water, but is soluble in alcohol and ether. It is an important reagent in organic work, being used to introduce the radical C_2H_5 into the place of other atoms or radicals. Ethyl iodide decomposes readily, especially on exposure even to diffused daylight, liberating iodine. When not exposed to light, the decomposition proceeds very slowly. This can be retarded further by the addition of a small quantity of a very dilute solution of sodium carbonate.

HIGHER MEMBERS OF THE PARAFFIN SERIES

46. Synthesis of Propane and Butane.—It has been shown how ethane was built up from methane. Propane and the higher members of the paraffin series are made synthetically in the same way. Thus, when ethyl iodide and methyl iodide are treated with sodium the following reaction takes place:

$$C_2H_5I+CH_3I+2Na=\underset{\text{propane}}{C_2H_5\cdot CH_3}+2NaI$$

In a similar manner butane is formed when propyl iodide and methyl iodide are treated with sodium:

$$C_3H_7I+CH_3I+2Na=\underset{\text{butane}}{C_3H_7\cdot CH_3}+2NaI$$

Butane can also be made by treating ethyl iodide with sodium:

$$2C_2H_5I+2Na=C_4H_{10}+2NaI$$

47. Naming of Compounds.—It has been shown how propane is made by linking the methyl radical with the ethyl radical. The formula for propane may therefore be written C_3H_8, which, however, does not show the structure of propane as does the formula $C_2H_5—CH_3$, or $C_2H_5\cdot CH_3$. The last two formulas show the ethyl and methyl groups linked together. Therefore, propane is also correctly called methyl ethane in accordance with a system by which any hydrocarbon of the paraffin series is regarded as being a methyl substitution product of the hydrocarbon just below it in the series. The formula for butane is C_4H_{10}, or $C_3H_7\cdot CH_3$, the latter formula showing it to be methyl propane.

48. A study of Table III will give an idea of the manner in which the formulas of the hydrocarbons of the paraffin series are written, and the various names that may be given to each hydrocarbon, according to the system of nomenclature used.

Compounds having a formula that consists of a series of hydrocarbon radicals linked together are called *open-chain hydrocarbons* as opposed to those having formulas that form a closed chain and are consequently known as *cyclic*, or *closed-chain, compounds*. Thus butane, $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$ is an example of open-chain compound.

TABLE III

NAMES AND FORMULAS OF HYDROCARBONS

Name of Hydrocarbon	Structural Formulas	Name of Radical	Formula of Radical
Methane	CH_4	Methyl	CH_3
Ethane or methyl methane	$CH_3\cdot CH_3$	Ethyl	C_2H_5
Propane or methyl ethane or dimethyl methane	$C_2H_5\cdot CH_3$ $CH_3\cdot CH_2\cdot CH_3$	Propyl	C_3H_7
Butane or methyl propane or diethyl	$C_3H_7\cdot CH_3$ $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$ $C_2H_5\cdot C_2H_5$	Butyl	C_4H_9
Pentane or methyl butane	$C_4H_9\cdot CH_3$ $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	Pentyl	C_5H_{11}
Ethyl propane	$C_3H_7\cdot C_2H_5$		
Hexane or methyl pentane	$C_5H_{11}\cdot CH_3$ $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	Hexyl	C_6H_{13}
Ethyl propyl methane	$C_2H_5\cdot CH_2\cdot C_3H_7$		

* * *

GENERAL FORMULAS

49. It has been previously pointed out that the formula of each compound listed in Table I differs from the one before and after it in the list, by CH_2. Therefore, if the number of carbon atoms in the formula is indicated by n the number of hydrogen atoms may be indicated by the expression $2n+2$.

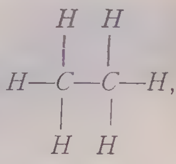
In other words, in the formulas of any of the hydrocarbons of the paraffin series there are twice as many hydrogen atoms, plus 2, as there are carbon atoms. For example in methane, CH_4 there is n or 1 carbon atom and $2n+2$ hydrogen atoms or $2n+2=4$, which is equivalent to 4 hydrogen atoms. In propane C_3H_8, $n=3$. Therefore, $2n=6$, and $2n+2=8$ hydrogen atoms. Thus, the general formula for a hydrocarbon of the paraffin series is C_nH_{2n+2}. The hydrocarbon radical contains one less hydrogen atom than does the hydrocarbon. Therefore the general formula for radicals of this series is C_nH_{2n+1}.

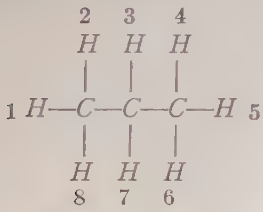
HOMOLOGOUS SERIES

50. In Table II the physical constants of the different compounds change uniformly and from the descriptions of the properties already given it is seen that the addition of CH_2 to each compound to form the next one in the series, exerts but little influence. Whenever the compounds of a series show a great resemblance in their chemical properties and a constant difference in composition between consecutive members, the series is said to be *homologous*. This fact is true of any class of derivatives that form homologous series. The relation is not a peculiarity of the paraffin series but it is true of many hydrocarbon series and their derivatives.

ISOMERISM

51. Meaning of Isomerism.—One of the most interesting peculiarities met with in the study of organic chemistry is the fact of the existence of a large number of compounds that contain the same elements in the same proportions, but which differ from one another either in their physical characteristics and in their chemical properties. This phenomenon is known as *isomerism*. Those compounds that have the same percentage composition, the same molecular weight, and show different physical and chemical properties, are termed *isomerides*, or *isomeric compounds*.

52. Isomerides Among Paraffins.—Up to and including propane, no isomeric compounds are known, but many are found higher in the series. In fact, the number of isomeric compounds possible increases as the compounds advance in the series. As each of the hydrogen atoms of methane bears the same relation to carbon, the properties of the product will be the same no matter which hydrogen atom is replaced by a given radical. Accordingly, as ethane is the methyl derivative of methane, there can be only one ethane. Now, as the graphic formula of ethane is  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$, and as all the hydrogen atoms bear the same relation to the molecule, it makes no difference which atom of hydrogen is replaced by the methyl radical to form propane; hence, there can be only one propane, and it is represented thus;



$$\begin{array}{ccccccccccc} & & & 2 & & 3 & & 4 & & & \\ & & & H & & H & & H & & & \\ & & & | & & | & & | & & & \\ 1 & H & - & C & - & C & - & C & - & H & 5 \\ & & & | & & | & & | & & & \\ & & & H & & H & & H & & & \\ & & & 8 & & 7 & & 6 & & & \end{array} \quad \text{or,} \quad CH_3{\cdot}CH_2{\cdot}CH_3$$

The hydrogen atoms have been numbered to distinguish between them in the discussion in the following articles.

53. Isomeric Propanes.—When methane and ethane were discussed it was shown that no matter what the method of formation, only one methyl chloride and one ethyl chloride could be obtained. This was attributed to the fact that all of the hydrogen atoms in methane and ethane are of equal value. In the case of propane, however, when chlorine or iodine replaces hydrogen, two compounds are formed which have either the formula C_3H_7Cl or C_3H_7I. In other words, it is possible to form two and only two propyl chlorides or two propyl iodides. As the result of the preparation of these two isomeric compounds of chlorine or of iodine, it can only be concluded that all of the hydrogen atoms of the propane molecule do not bear the same relation to the carbon atoms and that the hydrogen atoms are not of equal value. By referring to the formula for propane in which the hydrogen atoms are numbered, it is seen at once that the atoms numbered 3 and 7 bear a different relation to carbon than do the others, since each of them is linked to the middle carbon atom, which, in turn, is linked to only one other hydrogen atom and to two other carbon atoms. On the other hand each of the remaining hydrogen atoms, 1, 2, 4, 5, 6 and 8, is linked to a carbon atom, which, in turn, is linked to two other hydrogen atoms and to only one other carbon atom.

Therefore, if iodine replaces any of the hydrogen atoms numbered 1, 2, 4, 5, 6, or 8, a propyl iodide results having the formula $CH_3{\cdot}CH_2{\cdot}CH_2I$ or $CH_2I{\cdot}CH_2{\cdot}CH_3$, while if either 3 or 7 is replaced, a propyl iodide with the formula $CH_3{\cdot}CHI{\cdot}CH_3$ results. The first compound has a boiling point of 102° C. and a specific gravity of 1.78 and the second has a boiling point of 89° C. and a specific gravity of 1.74.

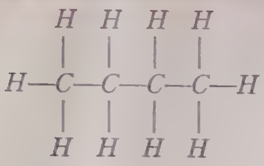
54. Isomeric Butanes.—Butane may be regarded as propane, in which one atom of hydrogen has been replaced by the methyl radical. It has just been explained that certain of the hydrogen atoms of propane bear different relations to the rest of the molecule than do the other hydrogen atoms, and it has been shown how this difference in relationship resulted in the formation of two isomeric propyl iodides. Consequently if either of the hydrogen atoms numbered 3 or 7 is replaced by a methyl radical, a butane is formed that is different from the butane formed when any of the remaining hydrogen atoms are replaced by the methyl group. Thus, when propyl iodide, $CH_3{\cdot}CH_2{\cdot}CH_2I$, is treated with methyl iodide and sodium, the following reaction takes place:

$$CH_3{\cdot}CH_2{\cdot}CH_2I+2Na+CH_3I=\underset{\text{butane}}{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3}+2NaI$$

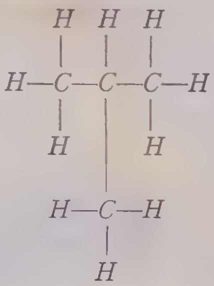
When propyl iodide, $CH_3{\cdot}CHI{\cdot}CH_3$, is treated in the same manner a different butane is obtained,

$$CH_3{\cdot}CHI{\cdot}CH_3+2Na+CH_3I=\underset{\text{butane}}{CH_3{\cdot}CH{\cdot}CH_3{\cdot}CH_3}+2NaI$$

The graphic formulas for these butanes are written,



and



The compound having the formula $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ boils at .3° C. and that with the formula $CH_3{\cdot}CH{\cdot}CH_3{\cdot}CH_3$ boils at −10.2° C.

55. Higher Isomerides.—As has been stated previously, the number of isomeric compounds possible increases as the number of carbon atoms in the compound increases. Thus, three isomeric pentanes are possible and they are known, and five hexanes, all of which are known. The point to be remembered is that as many isomeric compounds are possible as there are differently related sets of hydrogen atoms in the molecule of the hydrocarbon.

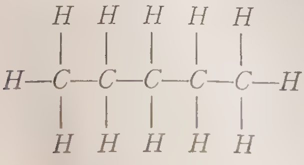
By applying the theory of isomeric compounds among the paraffins to the higher members of the series, it is shown that there are nine heptanes, five of which are known; and eighteen octanes, of which three are known. Besides there are nearly eight hundred hydrocarbons of the formula $C_{18}H_{38}$, of which only two or three are known. Very little is known regarding the higher members of the series.

56. Isomerism of Dihalogen Ethanes.—It has been shown that the four hydrogen atoms of methane can be replaced by halogen atoms and that the compounds formed are, CH_3X, CH_2X_2, CHX_3 and CX_4 in which X represents the halogen atom. Again, any one of the hydrogen atoms of ethane, C_2H_6, can be replaced by a halogen atom with the formation of an alkyl halide, but only one monohalogen compound of ethane for each of the halogens is known. Thus, there is only one monochlorethane, one monobromethane, and so forth.

When two atoms of a halogen are introduced into the ethane molecule, however, two isomeric dihalogen ethanes are formed, each having the formula $C_2H_4X_2$, or if the substituted halogen is chlorine, the formula will be $C_2H_4Cl_2$. One of these dichlorethanes is a symmetrical compound; that is, two hydrogen atoms, each connected to a different carbon atom, are replaced by chlorine. Its formula is $CH_2Cl{\cdot}CH_2Cl$. The other is an unsymmetrical compound, since two hydrogen atoms connected to one carbon atom are replaced by chlorine. Its formula is $CH_3{\cdot}CHCl_2$. The symmetrical compound is called *ethylene chloride*. It has a specific gravity of 1.2823 and boils at 83.7° C. The unsymmetrical compound is called *ethylidene chloride*. It has a specific gravity of 1.1863 and boils at 60° C. The exact constitution of these compounds can be proved by reactions involving unsaturated compounds. As is the case with methane, it is also possible to replace all of the hydrogen atoms of ethane with halogen atoms, the compounds $C_2H_3X_3$, $C_2H_2X_4$, C_2HX_5, and C_2X_6 being formed.

DEFINITIONS

57. Classes of Paraffins.—As carbon has a valence of 4, there can only be three ways in which the carbon atoms can be linked to one another to give rise to three main classes of isomerides. These are illustrated by the three classes of paraffin hydrocarbons: Primary or normal paraffins or those



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

FIG. 3

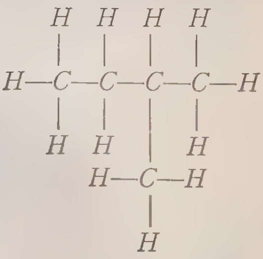


FIG. 4

in which no carbon atom is in combination with more than two others, a typical formula being given in Fig. 3; secondary paraffins, or those that have at least one carbon atom in combination with three others, the formula being given in Fig. 4; and tertiary paraffins, or those that have at least one carbon atom in combination with four others. The formula is given in Fig. 5.

The end, or terminal carbon atoms of Fig. 3 are each connected to only one other carbon atom, and for that reason they are known as primary carbon atoms. Each of the three middle carbon atoms, however, is connected to two other carbon atoms; therefore, they are known as secondary carbon atoms. When a carbon atom is linked to three other carbon atoms as shown in Fig. 4, it is known as a tertiary carbon atom, and when it is linked to four other carbon atoms, as is the center carbon atom in Fig. 5, it is termed a quaternary carbon atom.

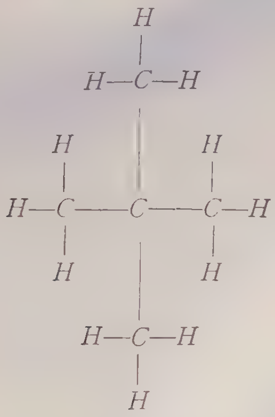
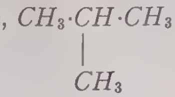


FIG. 5

58. Open-Chain Compounds.—The hydrocarbons so far treated have all been of the open-chain type. However, with the introduction of isomeric compounds, it becomes necessary to subdivide this class of compounds and to give each subdivision a new name. Thus, because of the appearance of the formula, open-chain compounds may also be either straight-chain or branched-chain compounds. For example, normal propyl iodide, $CH_3\cdot CH_2\cdot CH_2I$, and isopropyl iodide, $CH_3\cdot CHI\cdot CH_3$, are straight open-chain compounds. Again normal butane, $CH_3\cdot CH_2\cdot CH_2\cdot CH_3$, is a straight open-chain compound and secondary or isobutane,



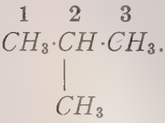
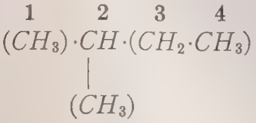
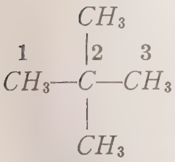
$CH_3\cdot \underset{\underset{CH_3}{|}}{CH}\cdot CH_3$

is an example of what is meant by a branched open-chain compound.

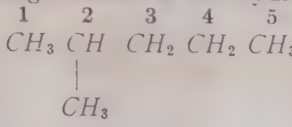
59. Systems of Nomenclature.—Numerous systems of nomenclature are used in naming the isomeric compounds met

TABLE IV

NAMES AND FORMULAS OF HYDROCARBONS

$CH_3\cdot CH_2\cdot CH_2I$	Normal, or primary, propyl iodide
$CH_3\cdot CHI\cdot CH_3$	Iso-, or secondary, propyl iodide
$CH_3\cdot CH_2\cdot CH_2\cdot CH_3$	Normal, or primary, butane
 $\overset{1}{CH_3}\cdot\underset{\underset{CH_3}{\vert}}{\overset{2}{CH}}\cdot\overset{3}{CH_3}$	Iso-, or secondary, butane Trimethylmethane 2-methyl propane
$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$	Normal, or primary, pentane
 $\overset{1}{(CH_3)}\cdot\underset{\underset{(CH_3)}{\vert}}{\overset{2}{CH}}\cdot(\overset{3}{CH_2}\cdot\overset{4}{CH_3})$	Iso-, or secondary, pentane Dimethylethylmethane... 2-methyl butane
 $\overset{1}{CH_3}—\underset{\underset{CH_3}{\vert}}{\overset{\overset{CH_3}{\vert 2}}{C}}—\overset{3}{CH_3}$	2-2-dimethyl propane Tetramethylmethane

with in organic chemistry. In these systems the carbon atoms in a chain may be numbered, thus, $\overset{1}{C}\cdot\overset{2}{C}\cdot\overset{3}{C}\cdot\overset{4}{C}\cdot\overset{5}{C}$, and the compound is considered a derivative of the hydrocarbon having the same number of carbon atoms as are present in the straight chain of the hydrocarbon to be named. The formula,



$$\overset{1}{CH_3}\ \underset{\substack{|\\ CH_3}}{\overset{2}{CH}}\ \overset{3}{CH_2}\ \overset{4}{CH_2}\ \overset{5}{CH_3}$$

contains six carbon atoms. It is, therefore, a hexane. The straight chain, however, represents pentane, and, according to this system, the compound is called 2-methyl pentane. In another system the linking of the carbon atoms to one another determines the name. Thus there are primary, secondary, and tertiary hydrocarbons. In still another system the name given to the hydrocarbon depends upon the derivation of the compound and the grouping of radicals in its formula. The different names for the same hydrocarbons by the systems mentioned are given in Table IV.

REAGENTS AND REACTIONS

60. Reagents Used in Organic Chemistry.—In organic chemistry it is frequently mentioned that certain compounds are formed as the result of the oxidation and reduction of other compounds. Therefore, an explanation of the preparation of the commoner reagents used will permit a mere reference to them when the reactions in which they are employed are discussed. Among the important oxidizing agents are nitric acid, potassium dichromate, chromium trioxide, and potassium permanganate. These compounds liberate nascent oxygen as shown by the following equations:

Nitric acid, HNO_3;

$$2HNO_3 = 3O + 2NO + H_2O$$

Potassium dichromate and sulphuric acid:

$$K_2Cr_2O_7 + 4H_2SO_4 = 3O + Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

Chromium trioxide and glacial acetic acid:

$$2CrO_3 + 6HC_2H_3O_2 = 3O + Cr_2(C_2H_3O_2)_6 + 3H_2O$$

Potassium permanganate in acid solution:

$$2KMnO_4 + 3H_2SO_4 = 5O + 2MnSO_4 + K_2SO_4 + 3H_2O$$

Potassium permanganate in alkaline solution:

$$2KMnO_4+KOH+H_2O=3O+2MnO_2+3KOH$$

The most commonly used acid reducing agents are:

Stannous chloride with hydrochloric acid:

$$SnCl_2+2HCl=SnCl_4+2H$$

Tin or iron with hydrochloric acid:

$$Sn+2HCl=SnCl_2+2H$$
$$Fe+2HCl=FeCl_2+2H$$

Zinc dust and glacial acetic acid:

$$Zn+2HC_2H_3O_2=Zn(C_2H_3O_2)_2+2H$$

Hydriodic acid:

$$2HI=I_2+2H$$

Under alkaline reducing agents may be grouped sodium amalgam with water and zinc dust with caustic soda. The reactions by which they liberate hydrogen are represented as follows:

$$NaHg+H_2O=NaOH+Hg+H$$
$$Zn+2NaOH=Na_2ZnO_2+2H$$

61. General Reactions.—The reactions commonly employed in building up the higher hydrocarbons and their derivatives from members lower in the series, are illustrated by the following equations:

The dry distillation of an alkali salt of a fatty acid with potassium hydroxide, sodium hydroxide, or with soda lime.

$$\underset{\text{potassium acetate}}{CH_3{\cdot}COOK}+KOH=CH_4+K_2CO_3$$

$$\underset{\text{sodium propionate}}{C_3H_7{\cdot}COONa}+NaOH=C_3H_8+Na_2CO_3$$

The reduction of alkyl halides with nascent hydrogen.

$$CH_3Cl+2H=CH_4+HCl$$
$$C_2H_5I+2H=C_2H_6+HI$$

The action of metallic sodium or zinc on alkyl halides.

$$2CH_3I+Zn=C_2H_6+ZnI_2$$
$$2C_2H_5I+2Na=C_4H_{10}+2NaI$$

The interaction of alkyl halides and zinc alkyl compounds.

$$2CH_3I+Zn(CH_3)_2=2C_2H_6+ZnI_2$$
$$2CH_3I+Zn(C_2H_5)_2=2C_3H_8+ZnI_2$$

62. Completed and Incompleted Reactions.—To show an important difference that commonly exists between inorganic and organic reactions, those reactions by which barium sulphate, $BaSO_4$, and ethyl bromide, C_2H_5Br, are formed will be taken for illustrative purposes.

When sulphuric acid or a solution of a soluble sulphate, such as sodium sulphate, is mixed with a solution of a barium salt, such as barium chloride, a precipitate of barium sulphate is formed. The equation representing the reaction that takes place is written with the molecular weights of each compound, as follows:

$$\overset{142.06}{Na_2SO_4}+\overset{208.29}{BaCl_2}=\overset{116.92}{2NaCl}+\overset{233.43}{BaSO_4}$$

This equation is interpreted to mean that when 142.06 parts by weight of sodium sulphate and 208.29 parts of barium chloride are brought together, 116.92 parts of sodium chloride and 233.43 parts of barium sulphate are formed. This is an illustration of a completed reaction and the quantity of sodium chloride or barium sulphate obtained, or the yield of either of these products is that indicated by the equation. In other words, the yield is *theoretical* and the reaction proceeds *quantitatively*.

63. In organic chemistry, reactions that go to completion or that proceed quantitatively are the exception rather than the rule. In one method of laboratory preparation of ethyl bromide, the equations representing the reactions that take place are written as follows:

$$\overset{46.058}{C_2H_5OH}+\overset{98.076}{H_2SO_4}=\overset{126.118}{C_2H_5HSO_4}+\overset{18.016}{H_2O}$$

$$\overset{126.118}{C_2H_5HSO_4}+\overset{119.02}{KBr}=\overset{108.97}{C_2H_5Br}+\overset{136.168}{KHSO_4}$$

These equations show an intermediate reaction product. They may be combined into one equation that will serve the present purpose. Thus,

$$\overset{46.058}{C_2H_5OH}+\overset{98.076}{H_2SO_4}+\overset{119.02}{KBr}=\overset{108.97}{C_2H_5Br}+\overset{136.168}{KHSO_4}+\overset{18.016}{H_2O}$$

According to the latter equation, if the reaction went to completion, it would only be necessary to use the parts of the compounds indicated by their molecular weights, or in the same proportion, in order to obtain the number of parts of the products indicated by the molecular weights. What would actually happen, however, if the molecular or theoretical proportions given were used, is that none of the reacting compounds would be completely used up and the reaction mixture would contain some of all of the reacting compounds, as well as some of all of the reaction products. The result would be a poor yield of the desired product, which, in this case, is ethyl bromide. To increase the yield, an excess over the theoretical quantity of certain of the reacting compounds is used, and naturally the least expensive compounds are chosen.

64. Of the materials used in the preparation of ethyl bromide, sulphuric acid and denatured alcohol are less expensive than potassium bromide. Therefore, an excess of alcohol and sulphuric acid above the theoretical quantity required are used in order to consume the more expensive potassium bromide. If then 100 grams of potassium bromide are used, the theory will call for $46:X::119:100$; $X=38.6$ grams of alcohol; and for $98:X::119:100$; $X=82.3$ grams of sulphuric acid.

In carrying out the experiment, however, approximately 100 grams of alcohol and 200 grams of sulphuric acid will be used for 100 grams of potassium bromide. The excess of alcohol used is then 61.4 grams or $61.4\times 100\div 38.6=159$ per cent. The excess of sulphuric acid used is 117.7 grams or 143 per cent. The theoretical yield of ethyl bromide based upon the quantity of potassium bromide used is

$$119:100::109:X$$
$$X=91.6 \text{ grams of ethyl bromide}$$

The actual yield obtained, however, will be only about 90 per cent. of the theoretical yield, or $91.6\times .90=82.4$ grams. Thus, the yield of ethyl bromide is stated to be about 90 per cent. of the theoretical.

ORGANIC CHEMISTRY

(PART 2)

DERIVATIVES OF SATURATED ALIPHATIC HYDROCARBONS

MONOHYDROXY ALCOHOLS

THEORETICAL CONSIDERATIONS

1. Introductory.—Although the monohydroxy* substitution products of the methane series, or the *alcohols*, as they are called, may be regarded as products resulting from the first step in the oxidation of the saturated aliphatic hydrocarbons of the methane series, they are not formed by the direct oxidation of these hydrocarbons. For the sake of simplicity, however, they are regarded as being derived from the paraffins by the substitution of the monovalent hydroxyl group, OH, for one atom of hydrogen. The general formula for the monohydroxy alcohols is, then, $C_nH_{2n+1}OH$ or $C_nH_{2n+2}O$. Two of the better known compounds of this class are wood alcohol and grain alcohol, so called because of their derivation. The chemical name for wood alcohol is *methyl alcohol*, and that for grain alcohol is *ethyl alcohol*.

---

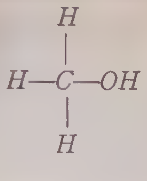
*Also called *monohydric*.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

2. Structure of Alcohol.—An analysis of methyl and ethyl alcohols shows them to have the percentage composition indicated by the formulas CH_4O and C_2H_6O, respectively. These formulas also show that carbon and hydrogen are present in exactly the same proportions as obtain in the case of methane and ethane. The structures of these simple hydrocarbons have already been proved, and in the treatment of the subject carbon was shown to be tetravalent and all of the hydrogen atoms to be of equal value. In the monohydroxy alcohols, however, a single atom of oxygen is present, and if carbon is to be tetravalent in these compounds, the existence of the monovalent hydroxyl group, OH or $-O-H$, must be proved. This can be done with the aid of certain reactions. Thus, when metallic sodium is brought in contact with an alcohol, hydrogen is evolved and a compound having the formula C_2H_5ONa and known as sodium alcoholate, sodium ethylate, or sodium ethoxide, is formed. If methyl alcohol is treated in this way, the compound formed is called *sodium methylate*, or *sodium methoxide*, CH_3ONa. The reaction that takes place is represented as follows:

$$CH_4O+Na=CH_3ONa+H$$

The reaction proceeds exactly as indicated by the equation; that is, if 23 parts or a gram-molecule of sodium is used, 1.008 parts or a gram-atom of hydrogen will be set free and no matter what the quantity of sodium and alcohol used, the quantity of hydrogen set free will always be in proportion to the foregoing figures. In other words, only one atom of hydrogen is ever removed from a monohydroxy alcohol by treating it with metallic sodium. This fact indicates that the hydrogen atoms in an alcohol are not all of equal value; for if they were, it should be possible to replace all of them by metallic sodium just as all of the hydrogen atoms of methane were replaced by chlorine. In inorganic chemistry the reason given for the fact that only certain hydrogen atoms of certain acids were replaceable was that these atoms were linked with oxygen. Therefore, in the case of an alcohol it may be assumed also that the hydrogen atom that is replaced by sodium is directly connected to the oxygen atom. In accordance with this assumption, the formula for methyl alcohol is written, CH_3OH, or graphically,



$$\begin{array}{c} H \\ | \\ H\text{—}C\text{—}OH \\ | \\ H \end{array}$$

3. A comparison of certain reactions between water and phosphorus trichloride, and the alcohols and phosphorus trichloride, furnishes additional proof of the structure of an alcohol. The formula for water is H_2O, or graphically, $H\text{—}O\text{—}H$, the latter formula indicating that the hydrogen atoms are of equal value and that water contains the hydroxyl group. When phosphorus trichloride is brought in contact with water, hydrochloric and phosphorous acids are formed. Thus,

$$3H_2O+PCl_3=3HCl+H_3PO_3$$

or, to simplify the equation,

$$3H-OH+PCl_3=3HCl+P(OH)_3$$

Thus it is seen that the hydroxyl groups of water have been replaced by chlorine, and that phosphorus has united with them to form phosphorous acid.

When a monohydroxy alcohol is treated with phosphorus trichloride, a similar reaction takes place that proves that the hydroxyl group exists in an alcohol. Thus,

$$3CH_3OH+PCl_3=3CH_3Cl+P(OH)_3$$

The synthesis of the alcohols from the alkyl halides provides further proof of the existence of the hydroxyl group. Thus, when methyl chloride is treated with a metallic hydroxide, such as potassium hydroxide or silver hydroxide, methyl alcohol is formed.

$$CH_3Cl+KOH=CH_3OH+KCl$$
$$CH_3Cl+AgOH=CH_3OH+AgCl$$

4. Names of Alcohols.—Since the aliphatic, monohydroxy alcohols are regarded as being derived from the saturated hydrocarbons of the methane series, by the substitution of the hydroxyl group for one atom of hydrogen, they also form a homologous series, some of the normal or primary members of which are given in Table I. The lower members of the series, according to the most commonly used system of nomenclature, take the name of the radical of the hydrocarbon to which they correspond. Thus, from methane, radical methyl, is obtained methyl alcohol. This compound may also be correctly called hydroxy methane or methyl hydroxide. The higher members of the series, however, have names that indicate the natural sources of the alcohol. According to another system, the final *e* of the hydrocarbon name is dropped and the ending *ol* added. Thus methane is also known as methanol. In still another system, methyl alcohol is given the name

TABLE I

NORMAL OR PRIMARY SATURATED ALCOHOLS

Name	Formula	Melting Point Degrees C.	Boiling Point Degrees C.	Specific Gravity Degrees C.
Methyl Alcohol	CH_3OH	− 97.1	64.57	.7964 at 15
Ethyl alcohol	C_2H_5OH	−114.1	78.40	.7850 at 25
Propyl alcohol	C_3H_7OH	−127.0	97.40	.8080 at 15
Butyl alcohol	C_4H_9OH	......	117.02	.8138 at 15
Pentyl or amyl alcohol	$C_5H_{11}OH$	......	137.80	.8168 at 20
Hexyl alcohol	$C_6H_{13}OH$	......	157.00	.8204 at 20
Heptyl alcohol	$C_7H_{15}OH$	− 36.5	175.80	.8300 at 16
Octyl alcohol	$C_8H_{17}OH$	− 17.9	195.50	.8375 at 0
Nonyl alcohol	$C_9H_{19}OH$	− 5.0	215.00	.8346 at 10
Decyl alcohol	$C_{10}H_{21}OH$	7.0	231.00	.8297 at 20
Dodecyl alcohol	$C_{12}H_{25}OH$	24.0	.....	....
Tetradecyl alcohol	$C_{14}H_{29}OH$	38.0	.....	....
Hexadecyl or cetyl alcohol	$C_{16}H_{33}OH$	50.0	.....	....
Octadecyl alcohol	$C_{18}H_{37}OH$	59.0	.....	....
Ceryl alcohol	$C_{27}H_{55}OH$	79.0	.....	....
Myricyl alcohol	$C_{30}H_{61}OH$	88.0	.....	....

carbinol, and all succeeding members of the series are regarded as carbinol in which one or more of the hydrogen atoms have been replaced by alkyl groups. The different names that may be correctly applied to the first five alcohols, together with their formulas, are given in Table II.

TABLE II

NAMES OF THE PRIMARY ALCOHOLS

Name	Formula	Formula of Carbinol
Methyl Alcohol	CH_3OH	
Hydroxy methane		
Methyl hydroxide		
Methanol		
Carbinol		CH_3OH
Ethyl Alcohol	C_2H_5OH	
Hydroxy ethane		
Ethyl hydroxide		
Ethanol		
Methyl carbinol		$(CH_3){\cdot}CH_2OH$
Propyl Alcohol	C_3H_7OH	
Hydroxy propane		
Propyl hydroxide		
Propanol		
Ethyl carbinol		$(CH_3{\cdot}CH_2){\cdot}CH_2OH$
Butyl Alcohol	C_4H_9OH	
Hydroxy butane		
Butyl hydroxide		
Butanol		
Propyl carbinol		$(CH_3{\cdot}CH_2{\cdot}CH_2){\cdot}CH_2OH$
Pentyl or Amyl Alcohol	$C_5H_{11}OH$	
Hydroxy pentane		
Pentyl hydroxide		
Pentanol		
Butyl carbinol		$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2){\cdot}CH_2OH$

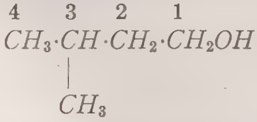
5. Isomeric Alcohols.—It has been explained how isomerism occurs in the saturated hydrocarbons of the methane series and that this isomerism is due to the branching of the hydrocarbon chain. One example was also given of an isomeric alkyl halide, namely, isopropyl iodide, and in this case it was shown that isomerism resulted because of the different positions taken in the hydrocarbon chain by the halogen atom. In the case of alcohols, isomerism also results by a simultaneous branching of the hydrocarbon chain and by changing the position of the hydroxyl group. The three ways in which isomerism may arise in the alcohols may be illustrated by five of the isomeric amyl alcohols. Formula **1** represents normal or primary amyl alcohol

$$\overset{5}{CH_3}\cdot\overset{4}{CH_2}\cdot\overset{3}{CH_2}\cdot\overset{2}{CH_2}\cdot\overset{1}{CH_2OH} \qquad (\mathbf{1})$$

By changing the position of the hydroxyl group, however, secondary amyl alcohol

$$\overset{5}{CH_3}\cdot\overset{4}{CH_2}\cdot\overset{3}{CH_2}\cdot\overset{2}{CHOH}\cdot\overset{1}{CH_3} \qquad (\mathbf{2})$$

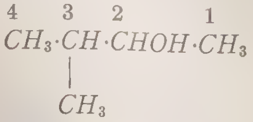
is obtained. In formula **3** the hydrocarbon chain branches which gives rise to another isomer. The hydroxyl group remains in the same position that it occupied in formula **1**.



$$\overset{4}{CH_3}\cdot\underset{\substack{| \\ CH_3}}{\overset{3}{CH}}\cdot\overset{2}{CH_2}\cdot\overset{1}{CH_2OH} \qquad (\mathbf{3})$$

This formula represents isoprimary amyl alcohol; iso, because of the branched chain; and primary because the hydroxyl group is linked to the carbon atom No. 1.

In formula **4** as compared with **1** there is simultaneous branching of the hydrocarbon chain and a difference in the position of the hydroxyl group as in formula **2**.

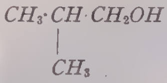
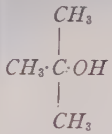
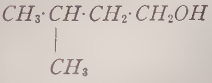
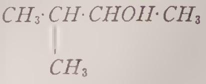
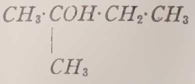
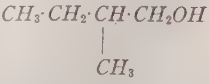
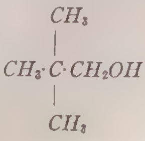


$$\overset{4}{CH_3}\cdot\underset{\substack{| \\ CH_3}}{\overset{3}{CH}}\cdot\overset{2}{CHOH}\cdot\overset{1}{CH_3} \qquad (\mathbf{4})$$

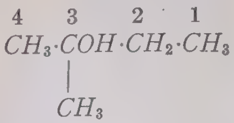
This compound is called isosecondary amyl alcohol because of the branched chain, and because the hydroxyl group is

TABLE III

ISOMERIC ALCOHOLS

Name	Formula	Boiling Point Degrees C.
Propyl alcohol . . . . (*Normal, primary propyl alcohol*)	$CH_3\cdot CH_2\cdot CH_2OH$	97.40
Isopropyl alcohol . . . . (*Secondary propyl alcohol*)	$CH_3\cdot CHOH\cdot CH_3$	82.85
Normal, primary butyl alcohol	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2OH$	117.00
Isobutyl alcohol . . . . (*Isoprimary butyl alcohol*)	 $CH_3\cdot\underset{CH_3}{\underset{\mid}{CH}}\cdot CH_2OH$	107.90
Normal, secondary butyl alcohol . . .	$CH_3\cdot CH_2\cdot CHOH\cdot CH_3$	100.00
Tertiary butyl alcohol	 $CH_3\cdot\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}\cdot OH$	83.00
Normal, primary amyl alcohol	$CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2OH$	137.80
Normal, secondary amyl alcohol . . . . (*Methyl propyl carbinol*)	$CH_3\cdot CH_2\cdot CH_2\cdot CHOH\cdot CH_3$	118.50
Isoprimary amyl alcohol . . . . (*Isoamyl alcohol*) (*Isobutyl carbinol*)	 $CH_3\cdot\underset{CH_3}{\underset{\mid}{CH}}\cdot CH_2\cdot CH_2OH$	131.00
Isosecondary amyl alcohol . . . . (*Methyl isopropyl carbinol*)	 $CH_3\cdot\underset{CH_3}{\underset{\mid}{CH}}\cdot CHOH\cdot CH_3$	112.00
Isotertiary amyl alcohol . . . . (*Dimethyl ethyl carbinol*)	 $CH_3\cdot\underset{CH_3}{\underset{\mid}{COH}}\cdot CH_2\cdot CH_3$	101.81
Active amyl alcohol . . . . (*Isoprimary amyl alcohol*)	 $CH_3\cdot CH_2\cdot\underset{CH_3}{\underset{\mid}{CH}}\cdot CH_2OH$	128.00
Diethyl carbinol . . . . (*Normal, secondary amyl alcohol*)	$CH_3\cdot CH_2\cdot CHOH\cdot CH_2\cdot CH_3$	117.00
Tertiary butyl carbinol . . . . (*Isoprimary amyl alcohol*)	 $CH_3\cdot\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}\cdot CH_2OH$	112.00

linked to the carbon atom No. 2. The fifth isomer is isotertiary amyl alcohol. Its formula is written,



$$\overset{4}{CH_3}\cdot\underset{\textstyle CH_3}{\overset{3}{COH}}\cdot\overset{2}{CH_2}\cdot\overset{1}{CH_3} \qquad (5)$$

It is called iso because of the branched chain and tertiary because the hydroxyl group is linked to the carbon atom No. 3.

6. In the foregoing explanation, with its accompanying illustrations, the carbon atoms have been numbered in order that it might be readily apparent just why certain different positions of the hydroxyl group gave rise to primary, secondary, and tertiary alcohols. Actually, however, these terms do not refer to the numbers given to the various carbon atoms, but to the grouping of the alkyl radicals in each compound. Thus, a primary alcohol is one in which the hydroxyl group is linked to a carbon atom that is in turn linked to only one other carbon atom. The general formula for this type of alcohol is $R\cdot CH_2OH$, in which R represents any alkyl radical. In a secondary alcohol the hydroxyl group is linked to a carbon atom that is directly connected to two other carbon atoms. The general formula is written, $\begin{matrix}R\\R\end{matrix}\!\!>CHOH$.

In a tertiary alcohol the hydroxyl group is linked to a carbon atom that is directly connected to three other carbon atoms. The general formula is $\begin{matrix}R\\R\\R\end{matrix}\!\!\rightarrow COH$.

The names, formulas, and boiling points of the isomeric alcohols, propyl, butyl, and amyl, or pentyl, are given in Table III.

GENERAL METHOD OF PREPARATION AND PROPERTIES

7. Preparation.—The synthesis of the first member of the series, namely, methyl alcohol, from an alkyl halide has already been treated in connection with the proof for the existence of the hydroxyl group in the alcohol structure. All of the alcohols of this series may be obtained in the same manner, but it is not to be thought that the synthetic processes used are of commercial value. These processes are of great value and interest only because by their use the probable structure of the alcohol is made evident. Enormous quantities of the lower alcohols are cheaply obtained from natural sources.

8. **Properties.**—In general, the alcohols may be compared with the metallic hydroxides, not only because they contain the hydroxyl group, but also because of the property they have, in common with the metallic hydroxides, of forming salts with acids, with the elimination of water. This similarity is shown by the following equations:

$$\underset{\text{methyl hydroxide}}{CH_3OH} + HNO_3 = \underset{\text{methyl nitrate}}{CH_3NO_3} + H_2O$$

$$\underset{\text{potassium hydroxide}}{KOH} + HNO_3 = \underset{\text{potassium nitrate}}{KNO_3} + H_2O$$

Just as an element unites with one, two, or more hydroxyl groups, depending on the valence of the element, so the hydrocarbon radical will unite with one or more hydroxyl groups, depending in this instance, on the number of hydrogen atoms removed from the hydrocarbon, as, for example, CH_3OH, $C_2H_4(OH)_2$, and $C_3H_5(OH)_3$.

METHYL ALCOHOL

9. **Manufacture of Methyl Alcohol,** CH_3OH.—On a commercial scale, methyl alcohol, or wood alcohol, is obtained as the result of the destructive distillation of wood in iron retorts connected with a condensing system. These retorts may be set either in a horizontal or a vertical position and are either rectangular or cylindrical in shape. The wood charged in the retorts varies in size. Thus it may be in 4-foot lengths, or it may be sawdust. After the retorts have been charged they are heated, the fuel used being that which is most easily and cheaply obtainable. When hard woods are subjected to destructive distillation the principal products obtained are charcoal, acetic or pyroligneous acid, acetates, acetone, and

wood alcohol. With the exception of the charcoal, all of these are found in the distillate.

10. The first step in the recovery of wood alcohol from the distillate consists in neutralizing with lime, the acetic acid present, calcium acetate being formed, and then distilling the neutralized liquor. The distillate in this case contains about 80 per cent. of wood alcohol, some acetic acid, acetone, and hydrocarbon oils. This distillate is now diluted with water to effect a separation of the hydrocarbon oils and some of the acetone, these substances forming an oily upper layer after the diluted distillate has been allowed to stand for a few days. The oily layer is then drawn off and the remaining liquid, which still contains some acetic acid and acetone, is distilled over lime.

Methyl alcohol boils at 64.57° C., and acetone at 56.48° C. Therefore, it is impossible to effect a complete separation of acetone from wood alcohol by fractional distillation, and other methods are resorted to. Thus, when the mixture of methyl alcohol and acetone is treated with calcium chloride, a crystalline compound of methyl alcohol and calcium chloride that is stable up to 100° C. is formed. The acetone distils below this temperature and a separation is thus effected. On adding water to the methyl alcohol and calcium chloride compound and raising the temperature slightly above 100° C., it decomposes and the methyl alcohol distils.

11. Oxalic acid may also be used for the purpose of purification, in which case the reactions that take place may be represented as follows:

$$2CH_3OH + \underset{\text{oxalic acid}}{H_2C_2O_4} = \underset{\text{methyl oxalate}}{(CH_3)_2C_2O_4} + 2H_2O$$

After allowing the solution to crystallize, the methyl oxalate is treated with ammonium hydroxide and the alcohol distilled, when the following reaction occurs:

$$(CH_3)_2C_2O_4 + 2NH_4OH = \underset{\text{ammonium oxalate}}{(NH_4)_2C_2O_4} + 2CH_3OH$$

12. Properties and Uses.—Pure methyl alcohol is a clear, colorless liquid, having a characteristic odor and a specific gravity of .7964 at 15° C. It boils at 64.57° C. and is very inflammable, burning with a pale blue, non-luminous flame. When taken into the system, it is extremely poisonous. It is miscible in all proportions with water, alcohol, and ether. It is used in the manufacture of dyes, for the denaturing of ethyl alcohol, and as a solvent for fats, oils, and resins.

ETHYL ALCOHOL

13. Manufacture of Ethyl Alcohol, C_2H_5OH.—Ethyl alcohol, or simply alcohol, as it is usually called, may be prepared synthetically by methods already described. On a commercial scale, however, it is obtained by the fermentation of sugar. The principal raw materials used for alcohol making are those which contain starch or sugar, but within the past few years alcohol has been successfully made on a commercial scale from wood. It has been established that fermentation is directly due to the action of certain chemical substances, called *enzymes*, on grape sugar or glucose. The particular enzyme that acts directly on glucose to produce alcohol, is called *zymase*. This enzyme is secreted by the yeast cell.

Beginning with starch or materials that contain starch, such as the different grains, potatoes, etc., it is necessary to convert the starch to sugar, or glucose, in order that fermentation may take place on the addition of yeast. This conversion is accomplished by the action of two enzymes called *diastase* and *maltase*, both of which are present in malt. The action of diastase on starch is to convert it into another sugar called maltose, which, in turn, is converted into glucose by the action of the enzyme maltase. When potatoes are used, they are treated with steam under pressure at about 150° C., thus being obtained in the form of a thin pulp. After cooling this pulp, malt is added and the temperature raised to 60° C., when the decomposition into maltose and glucose proceeds rapidly. After cooling to about 25° C., yeast is added to cause fermentaation, after the completion of which the *wash*, as it is called, is distilled. By using a fractionating column, alcohol of 90-per-cent. strength is obtained. The spent wash remaining in the still is used for feeding cattle.

The crude alcohol obtained is again subjected to careful fractionating when 95 per cent., alcohol, by volume, is obtained.

When a grain such as barley, corn, or rye is used, it is first allowed to germinate or sprout in a room kept at a temperature of about 60° C. In this way the enzymes present, diastase and maltase, convert the starch into sugar, after which, the grain is ground and sufficient water added to form a thin paste or *mash*. Yeast is then added and the mixture allowed to stand at 25° C., until fermentation is completed. The *wort*, as the mixture is now called, is then subjected to distillation.

14. Ordinary cane sugar, or *sucrose*, is not fermented by the action of zymase. However, some varieties of yeast contain an enzyme called *invertase*, that has the property of breaking sucrose up into two fermentable sugars, namely, glucose, or *dextrose*; and fructose, or *levulose*. A mixture of dextrose and levulose is called *invert sugar*. When molasses obtained from the manufacture of cane sugar is used as a raw material for alcohol manufacture, yeast is added and the sucrose converted into glucose and fructose, which are then acted on by zymase with the formation of alcohol.

15. Absolute Alcohol.—By absolute alcohol is meant 100 per cent. alcohol. The product obtained by the methods already described contains about 95 per cent. of C_2H_5OH and 5 per cent. of H_2O and to obtain absolute alcohol, the 95-per-cent. product is allowed to stand over quick-lime until all of the water has been removed by the lime. Thus,

$$CaO + H_2O = Ca(OH)_2$$

The dehydrated alcohol is then recovered or separated from the lime by distillation. The process of dehydration is greatly hastened by heating the alcohol and lime in a vessel equipped with a reflux condenser.

The presence or absence of water in alcohol may be shown by testing 1 or 2 cubic centimeters of it with anhydrous copper sulphate, which is white in color, in a test tube. If, when the alcohol is brought in contact with the copper sulphate, the latter resumes its blue color, water is present. If, however, the color of the anhydrous copper sulphate does not change, the absence of water is indicated. Anhydrous copper sulphate may be prepared by powdering a crystal about the size of a pea and then heating the powder in a small porcelain crucible to redness for about two minutes.

16. Alcohol From Wood Waste.—Wood has been mentioned as a raw material for making alcohol, and within recent years a process has been developed by which alcohol can be made from the waste of sawmills at a cost that makes the process of commercial value.

Wood consists principally of cellulose, a substance the exact structure of the molecule of which is as yet unknown. However, it has been established that cellulose belongs to that class of substances known as sugars. The action of acids on cellulose is to convert at least a part of it into fermentable sugars. Thus, when sawdust or other mill waste is digested with dilute sulphuric acid for 15 or 20 minutes, under a pressure of about 120 pounds per square inch, about 20 per cent. of the original wood is converted into sugars that are fermentable. The sugars are extracted from the digested material by treating it with water, while the sulphuric acid is neutralized by treating the solution with lime. The calcium sulphate thus precipitated is then allowed to settle, the clear solution removed to the fermenting tanks, allowed to cool to about 25° C., and then fermented.

The yield of alcohol obtained depends largely on the kind of wood waste used. In the present stage of development of the process, when hard-wood waste is the raw material used, the yield may vary from 6 gallons of 95 per cent. alcohol per ton of dry wood waste in the case of slippery elm to 14 gallons for silver maple. With soft-wood waste the yield varies from 20 gallons of alcohol per ton, when sugar-pine waste is used, to 26 gallons per ton with Western larch waste.

17. Properties of Ethyl Alcohol.—Pure ethyl alcohol is a transparent, colorless, limpid, inflammable liquid possessing a pleasant and characteristic odor and a burning taste. Its specific gravity is .7850 at 25° C. It boils at 78.4° C. and may be frozen to a solid that melts at −114.15° C. When ignited, ethyl alcohol burns with a pale non-luminous flame. Taken internally, in a concentrated form, it acts as a poison. Alcohol is used as a solvent for fats, oils, and gums. Large quantities are also used in the manufacture of ether, chloroform, celluloid, and smokeless powder, and in medicinal preparations.

INDUSTRIAL ALCOHOL

18. Proof Spirit.—Because of its extensive use in beverages, alcohol has been subjected to a heavy tax that would render its use in industry prohibitory. The tax is levied not on the actual strength or concentration of the alcohol but on its *proof spirit* content. By proof spirit is meant an alcohol-water solution containing 50 per cent. of C_2H_5OH by volume, or 42.7 per cent. by weight. Thus, 1 gallon of 100 per cent. alcohol is equivalent to 2 gallons of proof spirit, since each proof gallon contains 50 per cent. of C_2H_5OH by volume.

19. Denatured Alcohol.—In order to make alcohol cheaply available for use in industrial processes, denaturization is resorted to. Denaturization, in the case of alcohol, means to render it unfit for beverage purposes by the addition of certain specific and approved substances. The addition of these substances does not interfere with its proper use in industry since the manufacture is not confined to the use of alcohol that has been denatured according to any one certain formula. The kind of denaturant used depends in some cases on the uses to which the alcohol is to be put. Thus, if it is to be used in the manufacture of ether, it may contain sulphuric acid and ether as the denaturing agents. These will render the alcohol totally unfit for beverage purposes and at the same time aid rather than hinder in its industrial use. In most cases the denaturing agents used are those which are not easily separated from the alcohol. The following formulas for denatured alcohol have been approved by the United States Internal Revenue Bureau:

COMPLETELY DENATURED ALCOHOL

100 gallons ethyl alcohol	100 gallons ethyl alcohol
10 gallons methyl alcohol	2 gallons methyl alcohol
.5 gallon benzine	.5 gallon pyridine

Specially Denatured Alcohol

100 gallons ethyl alcohol	100 gallons ethyl alcohol
5 gallons methyl alcohol	1 gallon liquid pine tar
7 pounds camphor	

Completely denatured alcohol may be used for any purpose for which it is suitable, without restriction or payment of tax. Specially denatured alcohol is not subject to tax, but must be used under a permit and bond. Alcohol denatured according to the first formula given under Specially Denatured Alcohol, is used in the manufacture of celluloid, while that denatured according to the second formula may be used in the manufacture of liquid soap. Numerous other formulas for specially denatured alcohol, designed to meet the needs of different industries, exist.

HIGHER ALCOHOLS

20. Fusel Oil.—In the process of fermenting sugar to produce ethyl alcohol, a product known as fusel oil, which contains some of the higher alcohols, is recovered by fractionation from the first distillate obtained from the fermented liquid.

21. Normal Propyl Alcohol, $CH_3 \cdot CH_2 \cdot CH_2OH$.—Normal propyl alcohol, or propanol, is obtained from the fusel oil produced when sugars are fermented The largest yield is obtained from that fraction of fusel oil which boils between 85° C., and 110° C. This fraction is treated with phosphorus and bromine, the bromides of the alcohols present being formed, and from this mixture propyl bromide, which boils at 71.5° C., is easily separated by fractional distillation. The bromide is then treated with an alkali hydroxide, which gives the alcohol.

Normal propyl alcohol is a colorless liquid, with an odor resembling that of ordinary alcohol. It boils at 97.4° C., has a specific gravity of .8080 at 15° C., and is miscible with water in all proportions. The addition of calcium chloride to an aqueous solution of normal propyl alcohol causes it to separate. By oxidation it is converted into propionic aldehyde,* and on further oxidation into propionic acid; these reactions are indicated as follows:

---

*Aldehydes ketones, and acids are treated later in this Section.

$$C_3H_7{\cdot}OH \rightarrow C_2H_5{\cdot}COH \rightarrow C_2H_5{\cdot}COOH$$

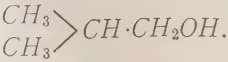
22. Isopropyl Alcohol, $CH_3{\cdot}CHOH{\cdot}CH_3$.—Isopropyl alcohol, or secondary propyl alcohol, like normal propyl alcohol, is a clear, colorless, liquid with an alcoholic odor. It boils at 82.85° C., has a specific gravity of .7898 at 15° C., and is miscible in all proportions of water, alcohol, and ether. It is obtained by reducing acetone with nascent hydrogen, and by treating isopropyl iodide with lead hydroxide. While the reactions of isopropyl alcohol show plainly that it is a hydroxide, oxidizing agents have a widely different effect on it than on any of the alcohols studied previously. When this compound is oxidized, it is converted into acetone, and upon further oxidation it does not yield an acid with the same number of carbon atoms, but breaks down into two simpler acids, namely, formic and acetic acids. These reactions are shown by the two following equations:

$$\underset{\substack{\text{isopropyl}\\\text{alcohol}}}{CH_3{\cdot}CHOH{\cdot}CH_3} + O = \underset{\text{acetone}}{CH_3{\cdot}CO{\cdot}CH_3} + H_2O$$

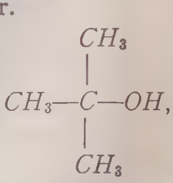
$$CH_3{\cdot}CO{\cdot}CH_3 + 3O = \underset{\substack{\text{formic}\\\text{acid}}}{HCOOH} + \underset{\substack{\text{acetic}\\\text{acid}}}{CH_3{\cdot}COOH}$$

23. Butyl Alcohols.—Theoretically, four butyl alcohols are possible, two being derived from each of the two butanes. All of these are known and two of them are primary alcohols.

Normal butyl alcohol has the formula $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, which shows that it is a primary alcohol. It is also known as *propyl carbinol*, and is prepared by the reduction of normal butyl aldehyde. This reduction is secured by means of nascent hydrogen obtained by the action of water on sodium amalgam. It is a limpid, colorless liquid, is highly refractive, and has a pleasant odor. It boils at 117° C., has a specific gravity of .811, and is soluble in alcohol. It is also soluble in water, to the extent of one part in twelve parts of water.

Isobutyl alcohol, or *fermentation butyl alcohol*, is also a primary alcohol, as is shown by its formula,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH{\cdot}CH_2OH$. This compound is frequently called *isoprimary butyl alcohol* to distinguish it from normal butyl alcohol. It is obtained from fusel oil. It is a colorless liquid with a specific gravity of .8061 at 15° C., an odor resembling that of fusel oil, and it boils at 107.9° C. It is soluble in alcohol and in ten times its own volume of water. It can be removed from its aqueous solution by the addition of nearly any water-soluble salt.

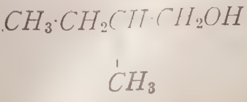
Normal secondary butyl alcohol, the third of the butyl alcohols, is a derivative of normal butane. It has the formula $CH_3{\cdot}CH_2{\cdot}CHOH{\cdot}CH_3$, and is frequently called *methyl ethyl carbinol*. This alcohol is prepared by reducing ethyl-methyl ketone with nascent hydrogen. It is a colorless, limpid liquid with a strong, agreeable odor, and a burning taste. It boils at 100° C., and has a specific gravity of .850. It is soluble in alcohol, but only slightly soluble in water.

Tertiary butyl alcohol has the structure  $CH_3\text{—}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{—}OH$, which results from a process of elimination, as three of the possible formulas have already been given the other butyl alcohols. The formula, however accords perfectly with the chemical behavior of the alcohol. Tertiary butyl alcohol is a white, prismatic compound with an odor resembling that of camphor. It melts at 25.5° C., boils at 83° C., and is soluble in alcohol and in water.

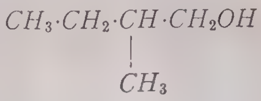
24. Amyl Alcohols.—The pentyl alcohols, or those containing five carbon atoms, are called amyl alcohols. Eight of these are possible and all are known. These may be divided into the following classes:

1. Four primary alcohols:

Normal primary amyl alcohol or
butyl carbinol.................. $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$

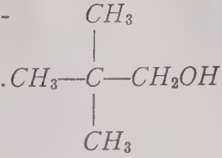
Isoprimary amyl alcohol; isoamyl
alcohol or isobutyl carbinol....  $CH_3{\cdot}CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H{\cdot}CH_2OH$

Active amyl alcohol or isoprimary amyl alcohol..................



$CH_3\cdot CH_2\cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2OH$

Tertiary butyl carbinol or isoprimary amyl alcohol.........

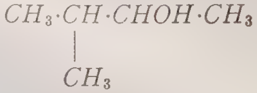


$CH_3—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}—CH_2OH$

2. Three secondary alcohols:

Normal secondary amyl alcohol or methyl propyl carbinol........ $CH_3\cdot CH_2\cdot CH_2\cdot CHOH\cdot CH_3$

Isosecondary amyl alcohol or methyl isopropyl carbinol.....

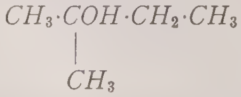


$CH_3\cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CHOH\cdot CH_3$

Diethyl carbinol or normal secondary amyl alcohol............ $CH_3\cdot CH_2\cdot CHOH\cdot CH_2\cdot CH_3$

3. One tertiary alcohol:

Isotertiary amyl alcohol or dimethyl ethyl carbinol.........



$CH_3\cdot \underset{\displaystyle CH_3}{\underset{|}{COH}}\cdot CH_2\cdot CH_3$

Isobutyl carbinol, or *amyl alcohol of fermentation*, is the most important member of the amyl group of alcohols It is obtained by the fractional distillation of the fusel oils from potatoes, beet roots, grapes, whiskey, etc The pure alcohol is a rather oily, colorless liquid with a specific gravity of .823; it boils at 131° C., and is somewhat soluble in water, one volume of the alcohol dissolving in fifty volumes of water.

Normal amyl alcohol is most easily prepared from caproic acid. It is a liquid boiling at 137.8° C., has a specific gravity of .829, has an odor resembling fusel oil, and is almost insoluble in water.

Active amyl alcohol, or *secondary butyl carbinol* is obtained with fermentation alcohol comprising about 13 per cent of it. It is a primary alcohol, as is shown by its formula.

Isotertiary amyl alcohol, or *dimethyl-ethyl carbinol*, is best obtained by shaking amylene, C_5H_{10} with sulphuric acid at $-20°$ C., and boiling with water. It is a mobile, colorless liquid, with an odor like that of camphor and has a similar taste. It has a specific gravity of .820, and is soluble in water, alcohol, ether, and chloroform.

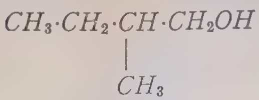
25. Effects of Oxidation on Alcohols.—The remaining amyl alcohols are of little importance. The differences existing between primary, secondary, and tertiary alcohols, and the effects of oxidation on them, may be stated as follows: *Primary alcohols* contain but one radical in combination with the group CH_2OH. *Secondary alcohols* contain two radicals in combination with the group $CHOH$. *Tertiary alcohols* contain three radicals in combination with the group COH.

Oxidation is a certain method for distinguishing between the classes of alcohols. The effects of oxidation may be briefly summed up thus: A primary alcohol yields on oxidation, first an aldehyde and then an acid containing the same number of carbon atoms as the original alcohol. A secondary alcohol, when treated with oxidizing agents, yields a ketone with the same number of carbon atoms as the original alcohol. A tertiary alcohol, under these conditions, yields neither an aldehyde nor a ketone, but decomposes yielding acids with a smaller number of carbon atoms.

An important point to remember is that when an organic compound undergoes oxidation, the molecule is attacked at the part that already contains oxygen; that is, where oxidation has already begun.

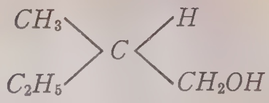
STEREOISOMERISM

26. Meaning of Stereoisomerism.—As any given structural formula represents only one compound and is the expression of a very definite set of properties, it follows that when two compounds are unlike, the differences that exist between them must be indicated by their structural formulas. Notwithstanding this fact, three isomeric amyl alcohols exist, which careful and thorough investigation has shown to have the same structural formula

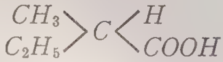


$$CH_3\cdot CH_2\cdot \underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2OH$$

or



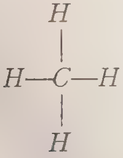
That this is true is proved by the fact that on being oxidized they yield valeric acid, the structure of which has been shown by synthesis to be



The three amyl alcohols with the same structural formula have the same chemical properties and nearly the same physical properties. However, there is one physical property that serves to distinguish them from one another. When a beam of polarized light is passed through these alcohols, its plane is turned to the right by one, to the left by another, and the third causes no rotation whatever. The first two are for this reason said to be *optically active*, while the third is *optically inactive*.

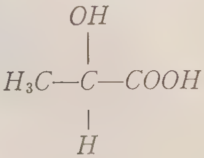
These three alcohols furnish a very good example of a form of isomerism known as *stereoisomerism*, which includes those compounds that have the same graphical formulas, conduct themselves in exactly the same way chemically, but differ in some of their physical properties, as in their action toward polarized light.

27. Explanation of Stereoisomerism.—The phenomenon of stereoisomerism is explained by the theory of Van't Hoff



$$\begin{array}{c} H \\ | \\ H\text{—}C\text{—}H \\ | \\ H \end{array}$$

FIG. 1



$$\begin{array}{c} OH \\ | \\ H_3C\text{—}C\text{—}COOH \\ | \\ H \end{array}$$

FIG. 2

and LeBel that the atoms or radicals in a molecule are arranged differently in space, but in order that a compound may show the property of stereoisomerism, it is absolutely necessary that the four bonds of the carbon atom hold in combination four different kinds of atoms or groups of atoms. A carbon atom exhibiting a linkage of this kind is known as an asymmetric carbon atom. Thus, in Fig. 1, which is the formula for methane, the carbon atom is not asymmetric, since it is not connected to four dissimilar atoms or groups of atoms. In Fig. 2, however, the carbon atom conforms to the definition and is asymmetric.

28. On inspection of the formula for the isomeric amyl alcohols it will be noted that the central carbon atom is connected to four different atoms and groups of atoms consisting of H, CH_3, C_2H_5, and CH_2OH. Therefore, this carbon atom is asymmetric, and if it is represented as occupying the center of a regular tetrahedron, as shown in Fig. 3 *(a)* and *(b)*, with the different atoms and radicals attached to the four corners, the difference in arrangement existing between *(a)* and *(b)* may be plainly seen. It will also be noted that each of these tetrahedrons is the mirror image of the other and, it is impossible to superimpose one upon the other and cause the positions of the same radical on each tetrahedron to coincide. In the case of a compound like methane, which possesses one carbon atom linked to four hydrogen atoms, only one arrangement of the atoms is possible. In the case of a compound containing an asymmetric carbon atom, however, two but only two dif-

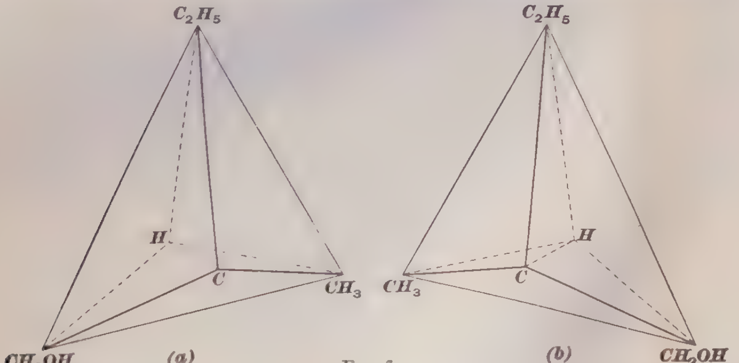


Fig. 3

ferent arrangements of the groups or atoms are possible. Thus, it is logical to assme that if a compound represented by the formula of Fig. 3 (*a*) turns the plane of polarized light to the right, or is dextrorotatory, its mirror image, or another compound of the same structural formula, but having its radicals and atoms arranged as in (*b*), will turn the plane of polarized light to the left, or is levorotatory. Again, if a compound consists of an equal number of both dextrorotatory and levorotatory molecules, it should be optically inactive. Furthermore, any compound containing one or more asymmetric carbon atoms should be active toward polarized light.

29. These points are easily demonstrated in the laboratory. The foregoing explanation of optical activity covers practically all cases, and it is believed that this phenomenon is always caused by some difference in the arrangement, in space, of the atoms and radicals composing optically active compounds. The theory of the asymmetric carbon atom is supported by a large number of facts, and nothing has as yet been brought forth to supplant it in the minds of chemists.

ALDEHYDES

30. Derivation of Name.—When a primary alcohol like ethyl alcohol, is brought in contact with a powerful oxidizing agent, such as results when potassium dichromate is mixed with sulphuric acid, a compound, the class name for which is *aldehyde*, is formed. An analysis of this aldehyde shows it to have the composition represented by the formula C_2H_4O. Thus, it contains two less hydrogen atoms than the alcohol from which it was derived. Hence the name *aldehyde*, which is derived from the words *alcohol dehydrogenatum*.

31. Structure of Aldehydes.—The reaction according to which alcohol is oxidized to an aldehyde is represented as follows:

$$C_2H_5OH+O=C_2H_4O+H_2O$$

The formula for ethyl alcohol shows that it contains six hydrogen atoms, while that of the corresponding aldehyde contains four. Therefore, in order to establish the constitution of the aldehyde, it is necessary to show which of the six hydrogen atoms of ethyl alcohol have been removed.

On treating an alcohol with metallic sodium or phosphorus trichloride, the existence of the hydroxyl group was proved. When an aldehyde is treated with metallic sodium, however, no reaction takes place, and this indicates the absence of the hydroxyl group. Again, when an aldehyde is treated with phosphorus pentachloride, the reaction that takes place is not similar to that which occurs when an alcohol is so treated. Thus,

$$C_2H_5OH + PCl_5 = C_2H_5Cl + HCl + POCl_3$$
$$C_2H_4O + PCl_5 = C_2H_4Cl_2 + POCl_3$$

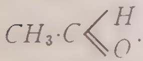
from which it is seen that the oxygen in the aldehyde is replaced by two atoms of chlorine with the formation of dichlorethane, $C_2H_4Cl_2$·, the structural formula of which is $CH_3{\cdot}CHCl_2$.

This compound may also be prepared by the action of chlorine on ethane, thus:

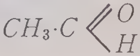
$$CH_3{\cdot}CH_3 + 2Cl_2 = CH_3CHCl_2 + 2HCl$$

Here it is seen that two atoms of hydrogen connected to one carbon atom have been replaced by chlorine. Therefore, when the oxygen of the aldehyde, C_2H_4O, is replaced by chlorine to form the same dichlorethane, it is logical to assume that this oxygen atom is directly connected to one of the carbon atoms; or, it occupies the same position in the aldehyde as do the two hydrogen atoms in ethane that are replaced by chlorine. This may be represented as follows:

$$CH_3{\cdot}CH_3 \ldots\ldots CH_3{\cdot}CHH_2 \ldots\ldots CH_3{\cdot}CHCl_2$$
$$C_2H_4O \ldots\ldots\ldots\ldots CH_3{\cdot}CHO \ldots\ldots\ldots\ldots CH_3{\cdot}CHCl_2$$

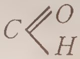
The structure of the aldehyde is thus shown to be $CH_3{\cdot}CHO$ or  $CH_3{\cdot}C\begin{matrix}\diagup H\\ \diagdown\!\!\diagdown O\end{matrix}$. The group, CO is called a *carbonyl group* or simply *carbonyl*.

32. Still further information is obtained concerning the structure of an aldehyde when the products formed by its oxidation are considered. Thus, an alcohol on oxidation is first converted into an aldehyde, which is an intermediate product, the final product of the oxidation being an acid. Ethyl alcohol has the formula $CH_3{\cdot}CH_2OH$, and yields, on oxidation, an acid $CH_3{\cdot}COOH$. The two hydrogen atoms removed by the oxidation must belong to the group CH_2OH, and only COH remains. Therefore two structural formulas are possible for the aldehyde,

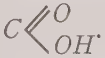


$CH_3{\cdot}C\begin{array}{l} /\!\!/ O \\ \backslash H \end{array}$ and $CH_3{\cdot}C{-}{-}OH$.

The second formula points to a hydroxyl group in aldehydes, but investigation has shown that the aldehydes do not possess the properties peculiar to substances containing this group, hence the second formula cannot be the correct one. As the second formula does not represent the aldehydes, the first one must be correct. This conclusion is supported by the fact that on oxidation the aldehydes yield acids, the group



$C\begin{array}{l} /\!\!/ O \\ \backslash H \end{array}$ being changed to



$C\begin{array}{l} /\!\!/ O \\ \backslash OH \end{array}$.

33. General Properties of Aldehydes.—The aldehydes are named after the acids into which they may be converted by further oxidation. They also form a homologous series, the first four members of which are given in Table IV, together with some of their properties. A general idea of the characteristics and various methods of preparation of the aldehydes will be obtained from a description of the most prominent members of this class of compounds, the reactions of which

TABLE IV

PROPERTIES OF ALDEHYDES

Name	Formula	Boiling Point Degrees C.	Specific Gravity Degrees C.
Formaldehyde....	$H{\cdot}CHO$	−21.0	.9172 at −21
Acetaldehyde.....	CH_3CHO	20.8	.7834 at 18
Propionaldehyde..	C_2H_5CHO	48.8	.8066 at 20
Butyraldehyde....	C_3H_7CHO	74.0	.8170 at 20

$OH_3OH + O = H\cdot C\lessdot^{H}_{O} + H_2O$

may be considered identical with those of the other aldehydes.

34. Formaldehyde, *H·CHO*.—Formaldehyde which is also called *methanal*, is formed when methyl alcohol is oxidized. It may be made by passing the vapor of methyl alcohol over heated platinum or copper. Commercially, it is prepared by passing the vapors of methyl alcohol mixed with air through a heated copper tube, the formaldehyde formed being absorbed in water. It is also made by the distillation of barium or calcium formates. Formaldehyde is also a product of the incomplete combustion of peat, wood, and a number of other organic compounds.

At ordinary temperatures formaldehyde is a gas having a very pungent odor; on cooling it forms a liquid that boils at −21° C. It is manufactured on a large scale and comes into the market in the form of a solution known as *formalin*. This solution contains about 40 to 42 per cent. of the formaldehyde gas by volume, and is a clear, colorless liquid with a pungent odor, and powerful antiseptic, bactericidal, and disinfectant properties. The solution has a specific gravity of 1.078 at 25° C., and is soluble in water and alcohol.

Formalin is used in surgery as an antiseptic. It is also used in the preservation of anatomical specimens, as it possesses the property of changing protein substances into hard, elastic masses, insoluble in water. It is also used in the manufacture of synthetic resins, aniline dyes, rubber goods, ink, sole leather, and in hardening skins, tanning, etc.

35. Paraformaldehyde, $(HCHO)_x$.—When a solution of formaldehyde is heated, or evaporated under diminished pressure, a white compound known as *paraformaldehyde* results. This compound melts at 162° C., and is soluble in water. It is used as a disinfectant.

36. Polymerization.—By polymerization is meant the formation from some simpler compound, of a new complex compound having the same percentage composition as the simple compound and a molecular weight that is an exact multiple of that of the simple compound. Thus, paraformaldehyde consists of an unknown number of molecules—probably two, in which case it would be represented by the formula, $(HCHO)_2$. It is known as a polymeride of formaldehyde.

An important point to be remembered in connection with the definition of polymerization is that a polymeride can be converted back into the original compound by simple means, such as by heating.

37. Metaformaldehyde, $(HCHO)_3$.—Metaformaldehyde, also called *trioxymethylene*, is formed by the polymerization of anhydrous liquid formaldehyde. It melts at about 60° C., and is soluble in water, alcohol, or ether. When heated with water it is converted into formaldehyde.

38. Acetaldehyde, CH_3CHO.—Acetaldehyde, also known as *ethanal*, is formed by the oxidation of ethyl alcohol. It is found in the crude alcohol obtained from raw materials such as potatoes, starch, and beet sugar.

Acetaldehyde is best prepared by distilling alcohol with potassium dichromate and sulphuric acid, thus:

$$\underset{\text{ethyl alcohol}}{CH_3{\cdot}CH_2OH}+O=\underset{\text{acetaldehyde}}{CH_3{\cdot}CHO}+H_2O$$

Another method of preparing acetaldehyde is by the dry distillation of a mixture of the acetate and formate of calcium, This reaction is as follows:

$$Ca(CH_3COO)_2+Ca(HCOO)_2=2CH_3CHO+2CaCO_3$$

39. Laboratory Preparation of Acetaldehyde.—Acetaldehyde may be prepared in the laboratory by the following method: A cold mixture consisting of 4 parts of concentrated sulphuric acid and 3 parts of alcohol is added drop by drop to 3 parts of coarsely powdered potassium dichromate, covered with 12 parts of water, and contained in a large flask *a*, Fig. 4, that is fitted with a dropping funnel *b* and a condenser *c* arranged as shown. The reaction may be started by warming the contents of the flask *a* over a water bath *d*, after which it proceeds vigorously. The acetaldehyde thus formed, together with some alcohol and water vapor, passes into the condenser *c*, which is kept cool with running water. As the vapor condenses, the greater part of the alcohol and water returns to the flask, but the aldehyde, being much more volatile, passes into the wide-mouthed receivers *e* and *f*, which are placed in a dish of ice water. These receivers are half filled with ether, which absorbs the aldehyde.

After the chemical action is over, the receivers *e* and *f* are disconnected at *g*, and are connected with an apparatus generating dry ammonia gas: this dried gas is then passed into the ethereal solution of the aldehyde to the point of saturation. When this point is reached, a beautiful crystallized compound of aldehyde-ammonia separates.

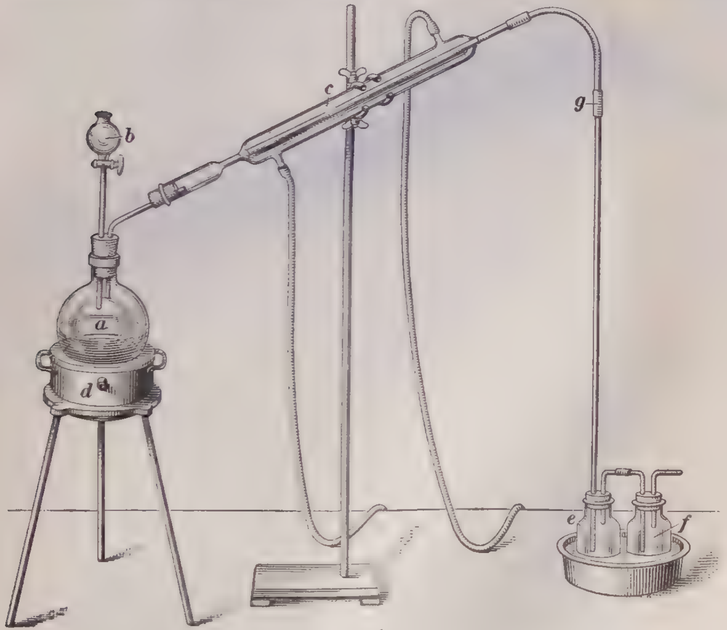
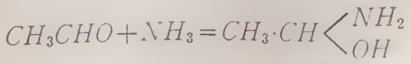


FIG. 4



$$CH_3CHO+NH_3=CH_3\cdot CH{<}\begin{matrix}NH_2\\ OH\end{matrix}$$

aldehyde ammonia

The ether is poured off and the crystals dried on filter paper. In the air these crystals gradually acquire a peculiar odor and become yellow. The crystals are then treated with dilute sulphuric acid, and on heating the mixture, the pure aldehyde distills and is condensed by ice-cold water.

$$CH_3{\cdot}CH\left\langle\begin{matrix}NH_2\\OH\end{matrix}\right.+H_2SO_4=CH_3CHO+NH_4HSO_4$$

During the purification of alcohol by filtering through charcoal, some of it is oxidized to aldehyde, and when afterwards distilled the *first running* or fraction, contains considerable aldehyde.

40. Properties of Acetaldehyde.—Acetaldehyde is a colorless, inflammable liquid, having a pungent, suffocating odor. It has a specific gravity of .7834 at 18° C., boils at 20.8° C., and solidifies at −123.6° C. It mixes in all proportions with water, alcohol, and ether. The most characteristic property of acetaldehyde is its power to unite directly with other substances. It is a strong reducing agent and combines readily with oxygen to form acetic acid;

$$CH_3{\cdot}CHO+O=CH_3{\cdot}COOH{\cdot}$$

When subjected to the action of reducing agents, such as sodium amalgam and water, acetaldehyde is converted into alcohol:

$$CH_3CHO+2H=CH_3{\cdot}CH_2OH$$

41. Paraldehyde, $(CH_3{\cdot}CHO)_3$.—Paraldehyde is a polymeride of acetaldehyde. It is formed by treating acetaldehyde with concentrated sulphuric acid. Above 12.5° C. it is a clear, colorless liquid having a pleasant but rather suffocating odor, and a sharp, burning taste. It boils at 124° C., has a specific gravity of .9943 at 20° C., is soluble in alcohol, ether, and water. Paraldehyde is used as an opiate, as an antidote for morphine, and to obviate the dangers of chloroform narcosis.

42. Metaldehyde, $(CH_3{\cdot}CHO)_3$.—Metaldehyde, a polymeride of acetaldehyde, is made in the same manner as paraldehyde, only a lower temperature is used. It crystallizes in needles, is insoluble in water, is slightly soluble in alcohol, and is completely soluble in chloroform. It is also known under the name of metacetaldehyde. It sublimes at 150° C., and when heated to 120° C. in a sealed tube, or when distilled with sulphuric acid, it is converted into aldehyde. Metaldehyde has the same molecular weight as paraldehyde.

43. Chloral, or Trichloraldehyde, $CCl_3{\cdot}CHO$.—The compound known as trichloraldehyde, or *chloral*, is of considerable importance owing to the therapeutic use of its hydrate. It was discovered in 1832 by Liebig, during the investigation of the action of chlorine upon alcohol. To prepare it, dry chlorine is passed into absolute alcohol. In the beginning the reaction mixture is artificially cooled, but when, after a few days, the reaction becomes less violent, the temperature is gradually raised to 100° C., the passage of chlorine being continued until it is no longer absorbed. Then itermediate products formed as the result of this chlorination process are: acetaldehyde, $CH_3{\cdot}CHO$; acetal, $CH_3{\cdot}CH(OC_2H_5)_2$; dichloracetal, $CHCl_2{\cdot}CH(OC_2H_5)_2$; and trichloracetal, $CCl_3{\cdot}CH(OC_2H_5)_2$. The final products are: chloral alcoholate, $CCl_3{\cdot}CH(OC_2H_5)OH$; chloral hydrate, $CCl_3{\cdot}CH(OH)_2$, and trichloracetal. This mixture is treated with concentrated sulphuric acid, chloral being obtained.

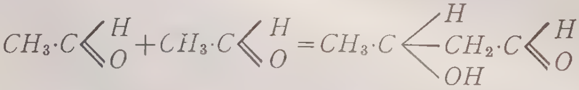
44. Properties of Trichloraldehyde.—Trichloraldehyde is a colorless, mobile liquid, having a pungent odor. It boils at 97.7° C., and has a specific gravity of 1.512 at 20° C. If it is allowed to stand in contact with water, an energetic action takes place and the easily soluble *chloral hydrate*, $CCl_3{\cdot}CH(OH)_2$ separates in transparent, colorless crystals, or in a flat, white, crystalline mass. This hydrate is sold under the name of chloral. It has a peculiar pungent odor and taste, melts at 57° C., and boils at 97.5° C., breaking up into chloral and steam, but reforms again on cooling.

Chloral hydrate is soluble in water, alcohol, ether, and chloroform, imparting to these solutions its odor and taste. When taken internally it produces sleep. As chloral hydrate does not show the aldehyde reactions, it has been given the formula $CCl_3{\cdot}CH\genfrac{<}{}{0pt}{}{OH}{OH}$; it is one of the few known compounds containing two hydroxyl groups in union with a single carbon atom. Treated with caustic potash, both chloral and chloral hydrate break up, yielding chloroform and potassium formate, thus:

$$CCl_3\cdot CHO + KOH = CHCl_3 + HCOOK$$

On account of its purity, chloroform prepared in this manner is preferred for use as an anesthetic.

45. Aldol, $(C_2H_4O)_2$.—On adding a dilute solution of potassium hydroxide or zinc chloride to acetaldehyde, a compound called aldol is formed. This compound has the same percentage composition as does acetaldehyde, but its molecular weight is twice that of the latter. Therefore, the empirical formula of aldol is $(C_2H_4O)_2$. The reaction that takes place in its formation is represented as follows:



$$CH_3\cdot C\Big\langle{}^{H}_{O} + CH_3\cdot C\Big\langle{}^{H}_{O} = CH_3\cdot C\left\langle\begin{matrix}H\\ CH_2\cdot C\Big\langle{}^{H}_{O}\\ OH\end{matrix}\right.$$

From its structural formula it is seen that aldol must exhibit the properties of both an alcohol and an aldehyde; hence its name. Aldol is a polymeride of acetaldehyde, but, since it cannot be converted to acetaldehyde by simple means, it is called a *condensation product*. By condensation in this case is meant the union of two or more molecules of a compound to form a new compound having a molecular weight that is a multiple of that of the original compound, but which cannot be easily converted into the original compound. In other words, condensation is a form of polymerization, the two terms being used to indicate that the compound is easily or with difficulty converted back into the original compound.

Aldol is a syrupy liquid, soluble in water, alcohol, and ether. It has a specific gravity of 1.1094 at 16° C. When heated under atmospheric pressure it decomposes with the formation of crotonaldehyde, $CH_3\cdot CH{:}CH\cdot CHO$, an unsaturated compound that will be discussed later.

46. Tests for Aldehydes.—Aldehydes may be detected by the following tests:

1. When a solution of magenta is decolorized by means of sulphurous acid, its red color is restored by an aldehyde.

2. Aldehydes are resinified by alkalies. Thus, when an aqueous solution of acetaldehyde is treated with a concentrated solution of potassium hydroxide, and the mixture warmed, an amorphous precipitate is obtained. This precipitate is called *aldehyde resin.*

3. When an ammoniacal silver solution is treated with an aldehyde and the mixture warmed, a beautiful metallic silver mirror is deposited upon the sides of the vessel containing the solution. The ammoniacal silver solution is made by adding a slight excess of caustic potash to a silver-nitrate solution, and just enough ammonium hydroxide to dissolve the silver oxide precipitated by the caustic-potash.

KETONES

47. Introductory.—It already has been stated that on oxidation primary alcohols yield aldehydes and secondary alcohols yield ketones, and that, as a rule, when an organic compound containing oxygen is submitted to further oxidation, the molecule is attacked at that point where oxygen is already present. Thus, when normal propyl alcohol, $CH_3{\cdot}CH_2{\cdot}CH_2OH$ is oxidized, propionaldehyde, $CH_3{\cdot}CH_2{\cdot}CHO$, is obtained; and when isopropyl alcohol, $CH_3{\cdot}CHOH{\cdot}CH_3$, is oxidized, a compound having the same molecular weight but different properties than propionaldehyde is formed. The empirical formula of this compound is C_3H_6O. It is the lowest member of a class of compounds called ketones and the name by which it is known is *acetone.*

48. Structure of Ketones.—A study of the conduct of acetone will readily show that this compound resembles the aldehydes more closely than any other body thus far considered. It is neither an alcohol nor an acid, as it acts entirely different from either of these bodies. When treated with phosphorus pentachloride, the oxygen atom of acetone is replaced by two chlorine atoms, dichlorpropane, $CH_3{\cdot}CHCl_2{\cdot}CH_3$, being formed, while on reduction with nascent hydrogen, acetone forms isopropyl alcohol, $CH_3{\cdot}CHOH{\cdot}CH_3$, from which acetone is again obtained by oxidation. As in the case of the aldehydes, the reaction with phosphorus pentachloride indicates the presence of the carbonyl group in acetone and since, in the case of the formation of an aldehyde by the oxidation of a primary alcohol, two hydrogen atoms are removed from the CH_2OH group, it is logical to assume that in the case of a secondary alcohol the two hydrogen atoms are removed from the $CHOH$ group. Thus, $CH_3 \cdot CHOH \cdot CH_3 - 2H = CH_3 \cdot CO \cdot CH_3$, which gives the accepted formula for acetone.

The ketones form a homologous series, the second and third members of which are diethyl ketone, $C_2H_5 \cdot CO \cdot C_2H_5$, and dipropyl ketone, $C_3H_7 \cdot CO \cdot C_3H_7$.

49. Preparation and Properties of Acetone.—Large quantities of acetone are recovered by the fractional distillation of crude wood spirits or by the dry distillation of calcium acetate, thus:

$$(CH_3 \cdot COO)_2Ca = CH_3 \cdot CO \cdot CH_3 + CaCO_3$$

The vapors given off in this distillation are condensed and the liquid obtained is again distilled with an excess of calcium chloride.

Acetone is a clear, colorless liquid, having a fragrant mint-like odor, and a sharp biting taste. Its specific gravity is .790 at 15° C. and it boils at 56.5 C. It is soluble in all proportions of water, alcohol, ether, and volatile oils. Acetone is highly inflammable and burns with a luminous flame. It is used as a solvent for gums and resins, and in the manufacture of smokeless powder, celluloid, and chloroform.

MONOBASIC ACIDS

PROPERTIES AND STRUCTURE

50. General Properties.—Organic acids of the methane series are the second oxidation products of the primary alcohols and may be considered as derived from the hydrocarbons, by the substitution of one or more $COOH$ groups for an equal number of hydrogen atoms. The basicity of these acids is

TABLE V

PROPERTIES OF FATTY ACIDS

Name of Acid	Formula	Boiling Point Degrees Centigrade	Melting Point Degrees Centigrade	Specific Gravity Degrees Centigrade	Natural Source
Formic	$H \cdot COOH$	100.47	8.35	1.2178 at 20°	Red ants and nettles
Acetic	$CH_3 \cdot COOH$	118.10	16.68	1.0492 at 20°	Vinegar
Propionic	$C_2H_5 \cdot COOH$	140.70	−19.30	.9870 at 20°	Oxidation of oils
Butyric	$C_3H_7 \cdot COOH$	162.30	−3.12	.9519 at 19°	Rancid butter
Valeric	$C_4H_9 \cdot COOH$	186.40	−58.50	.9415 at 20°	Valerian root
Caproic	$C_5H_{11} \cdot COOH$	205.00	−5.20	.9220 at 20°	Rancid butter
Œnanthylic	$C_6H_{13} \cdot COOH$	222.40	−10.50	.9212 at 15°	Oxidation of castor oil
Caprylic	$C_7H_{15} \cdot COOH$	237.50	16.50	.9185 at 18°	Rancid butter
Pelargonic	$C_8H_{17} \cdot COOH$	251.00	12.50	.9100 at 14°	Geranium leaves
Capric, or rutic	$C_9H_{19} \cdot COOH$	268.40	31.30	.9300 at 37°	Rancid butter
Undecylic	$C_{10}H_{21} \cdot COOH$	212.50	29.30		Oil of rue
Lauric	$C_{11}H_{23} \cdot COOH$	225.00	48.00	.8642 at 60°	Bayberries
Tridecylic	$C_{12}H_{25} \cdot COOH$	236.00	40.50		Coconut oil
Myristic	$C_{13}H_{27} \cdot COOH$	250.50	53.80	.8622 at 54°	Nutmeg butter
Pentadecylic	$C_{14}H_{29} \cdot COOH$	257.00 At 100 mm.	55.00		Agaricus integer (a fungus)
Palmitic	$C_{15}H_{31} \cdot COOH$	271.00	63.40	.8465 at 76°	Palm oil
Margaric	$C_{16}H_{33} \cdot COOH$	277.00	59.90	.8532 at 60°	
Stearic	$C_{17}H_{35} \cdot COOH$	291.00	69.32	.8428 at 80°	Tallow
Nondecylic	$C_{18}H_{37} \cdot COOH$	297.00	66.50		
Arachidic, or butic	$C_{19}H_{39} \cdot COOH$		77.00		Butter; earthnut
Nardic	$C_{20}H_{41} \cdot COOH$				Beef fat
Behenic	$C_{21}H_{43} \cdot COOH$		84.00		Oil of ben
Lignoceric	$C_{23}H_{47} \cdot COOH$		80.00		Beech-wood tar
Hyænic	$C_{24}H_{49} \cdot COOH$		77.00		Hyæna fat
Cerotic	$C_{26}H_{53} \cdot COOH$		82.50		Beeswax
Melissic	$C_{29}H_{59} \cdot COOH$		91.00		Beeswax

limited by the number of $COOH$ groups they contain. The hydrogen of this group is replaced in the formation of salts. A list of the commoner acids, together with some of the higher members of the series, their properties, and sources, is given in Table V. These acids are also called the *fatty acids*, because some of the higher members are found in fats. The lower members of the series do not occur in fats and are liquids at the ordinary temperature. They can be distilled without decomposition and have pungent odors. They are soluble in water, have strong acid properties, and crystallize at low temperatures. The members from butyric acid to pelargonic acid are oily liquids with unpleasant rancid odors and are only slightly soluble in water. The higher members, beginning with capric acid, are insoluble solids that cannot be distilled at atmospheric pressure without decomposition. They are odorless, do not possess as strongly developed acid properties as do the lower members, and resemble paraffin wax in character. All the acids of this series are soluble in alcohol and ether and, except formic acid, are very stable toward oxidizing agents.

51. Structure of Monobasic Acids.—The first two members of the series are formic acid and acetic acid, with the percentage compositions indicated by the empirical formulas CH_2O_2 and $C_2H_4O_2$, respectively. The structures of these acids and the others which make up the series may be proved by synthesis and numerous reactions. Thus, acetic acid is obtained by the oxidation of ethyl alcohol, as follows:

$$CH_3{\cdot}CH_2OH+O_2=C_2H_4O_2+H_2O$$

Since oxidation begins with the CH_2OH group, or at that point in the molecule where oxygen is already present, and because the acid also contains two carbon atoms, it is believed that the union between the carbon atoms in an acid is the same as that existing between the carbon atoms of an alcohol. It is logical to assume, therefore, that the CH_3 group exists in acetic acid, and, according to this assumption, its formula may be written $CH_3{\cdot}CO_2H$. Again, when acetic acid is acted on by phosphorus pentachloride, the same products are formed as when an alcohol is acted on by this reagent. Thus,

$$CH_3{\cdot}CO_2H+PCl_5=CH_3{\cdot}COCl+POCl_3+HCl$$

This reaction indicates the presence of the hydroxyl group in acetic acid and the formula may again be modified to $CH_3{\cdot}CO{\cdot}OH$. Further proof of the existence of the hydroxyl group is given by the action of metals on acetic acid. Thus, when acetic acid is brought in contact with sodium, one atom of hydrogen is replaced, and that the replaced hydrogen atom comes from the hydroxyl group, may easily be shown. Thus, when chlorine acts on acetic acid, three hydrogen atoms are successively replaced, the final product being trichloracetic acid. Now, if this compound is treated with phorphorus pentachloride, the presence of the hydroxyl group in it is shown. This indicates that the three hydrogen atoms of the methyl group in acetic acid have been replaced by chlorine, and that the hydrogen atom connected to oxygen is the one that is replaced by metals, since the compound $CCl_3{\cdot}COONa$ is known. The general formula for the acids of this series is then $R{\cdot}CO{\cdot}OH$, or simply $R{\cdot}COOH$. The $COOH$ group is known as the *carboxyl group*.

FORMIC ACID

52. Preparation.—Formic acid, $H{\cdot}COOH$, occurs naturally in red ants and in nettles, and when either of these is macerated in water and the resulting liquid distilled, the distillate obtained contains a small quantity of formic acid. Chemical methods for the preparation of formic acid are numerous. The following are of most interest:

1. By the oxidation of methyl alcohol or formaldehyde,

$$CH_3OH+2O=H{\cdot}COOH+H_2O$$
$$H{\cdot}CHO+O=H{\cdot}COOH$$

2. By heating hydrocyanic acid, HCN, with solutions of alkalies or mineral acids,

$$HCN+KOH+H_2O=NH_3+H{\cdot}COOK$$
$$HCN+HCl+2H_2O=NH_4Cl+H{\cdot}COOH$$

3. By the action of an alcoholic solution of potassium hydroxide on chloroform,

$$CHCl_3+4KOH=H\cdot COOK+3KCl+2H_2O$$

On distillation of the potassium formate with dilute sulphuric acid free formic acid is obtained,

$$H\cdot COOK+H_2SO_4=H\cdot COOH+KHSO_4$$

4. By the action of carbon monoxide on caustic potash,

$$KOH+CO=H\cdot COOK$$
$$H\cdot COOK+HCl=H\cdot COOH+KCl$$

5. By the action of metallic potassium on carbon dioxide in the presence of water,

$$2K+2CO_2+H_2O=H\cdot COOK+KHCO_3$$

53. Details of the laboratory preparation of formic acid from glycerol, $C_3H_5(OH)_3$, and oxalic acid, $H_2C_2O_4\cdot 2H_2O$, are as follows: A mixture of 30 grams of crystallized oxalic acid and 200 cubic centimeters of glycerol is heated to about 90° C. in a 500 cubic-centimeter flask provided with a thermometer and connected to a condenser. As a result of the reaction that takes place, formic acid, together with glycerol formate or monoformin, water, and carbon dioxide, is formed. The reaction takes place in two steps and may be represented as follows:

$$H_2C_2O_4\cdot 2H_2O=H\cdot COOH+CO_2+2H_2O$$
$$C_3H_5(OH)_3+H\cdot COOH=\underset{\text{monoformin}}{C_3H_5(OH)_2\cdot O\cdot CHO}+H_2O$$

When the evolution of carbon dioxide ceases, a fresh quantity of oxalic acid may be added and the operation continued, the same glycerol being used for the conversion of a large quantity of oxalic acid.

In this process of preparing formic acid, the acid first produced changes the glycerol into *monoformin*. The water of crystallization of the oxalic acid then decomposes the monoformin reconverting it into glycerol with the formation of additional formic acid, thus:

$$C_3H_5(OH)_2\cdot O\cdot CHO+H_2O=C_3H_5(OH)_3+H\cdot COOH$$

54. In order to prepare anhydrous formic acid from the product obtained as just described, the mixture of glycerol, water, and formic acid is first warmed with litharge and then heated to boiling. When additional quantities of litharge are no longer dissolved, the solution is filtered hot and the filtrate evaporated almost to dryness. On cooling, crystals of lead formate $Pb(H{\cdot}COO)_2$ are deposited. The lead formate is dried and powdered, and all but a very little is heated in a glass tube connected with a condenser. A current of dry hydrogen-sulphide gas is then passed through the hot tube and a reaction takes place between it and the lead formate, as the result of which formic acid is formed. Thus:

$$Pb(H{\cdot}COO)_2 + H_2S = PbS + 2H{\cdot}COOH$$

The anhydrous formic acid that collects in the receiver is then distilled with the small quantity of lead formate that was reserved, in order to remove traces of hydrogen sulphide gas.

55. Properties.—Pure formic acid is a clear, colorless liquid above 9° C., but a clear solid below this temperature, crystallizing in large brilliant plates. It has a specific gravity of 1.22 and boils at 101° C. It has a pungent odor and very corrosive action, attacking the skin and producing extremely painful sores. It is miscible in all proportions of water, alcohol, and ether, its water solution resembling acetic acid in taste and odor.

Formic acid is distinguished from its homologues by its reducing power and by the ease with which it is decomposed into water and carbon monoxide. When heated with the oxides of mercury or silver, the corresponding formates are formed, which, upon further heating, decompose, liberating the metal and setting free half the formic acid in the salt. This reaction is shown by the equation

$$2H{\cdot}COOAg = 2Ag + H{\cdot}COOH + CO_2$$

Warmed with concentrated sulphuric acid, formic acid decomposes, thus:

$$H{\cdot}COOH = H_2O + CO$$

Like other acids, formic acid neutralizes bases and forms salts. Being a monobasic acid it forms salts of the following general formulas, $H{\cdot}COOM$, $(H{\cdot}COO)_2M$, $(H{\cdot}COO)_3M$, etc.

in which M represents any monovalent, divalent, or trivalent metal. All the formates are soluble in water, and some of them crystallize very well. When distilled with concentrated sulphuric acid, they give off carbon monoxide, leaving a residue of sulphate.

Among the characteristic formates are *ammonium formate*; $H \cdot COONH_4$, which crystallizes in colorless, monoclinic crystals; *barium formate*, $(H \cdot COO)_2Ba$, which crystallizes in colorless, transparent rhombic prisms; *copper formate*, $(H \cdot COO)_2Cu$, which forms magnificent blue prisms; *iron formate* $(H \cdot COO)_3Fe$, which is a red powder; and *lead formate* $(H \cdot COO)_2Pb$, which forms long colorless needles.

ACETIC ACID

56. Manufacture of Acetic Acid, $CH_3 \cdot COOH$.—Acetic acid is the most important member of the group of fatty acids. It is found in nature combined with alcohols in the juices of plants. It was known to the ancients under the name of *wine vinegar*. As previously stated under methyl alcohol, the distillate obtained when wood is destructively distilled contains acetic acid. This distillate is neutralized with lime and the calcium acetate formed is obtained as a residue after the methyl alcohol and acetone have been distilled off. The calcium acetate is freed from tar by heating it in the presence of air to about 200° C. It is then treated in copper vessels with hydrochloric acid, which sets the acetic acid free, after which it is distilled.

$$Ca(CH_3 \cdot COO)_2 + 2HCl = 2CH_3 \cdot COOH + CaCl_2$$

The impure acetic acid thus obtained is purified by distilling it over potassium dichromate, which oxidizes any organic matter that may be present. Acetic acid is also manufactured on a commercial scale by subjecting dilute alcoholic solutions to fermentation and oxidation. The resulting solution of acetic acid is concentrated by fractional distillation.

57. Glacial Acetic Acid.—The acetic acid obtained by the foregoing methods always contains some water, which may be removed by subjecting the strong acid to temperatures above the freezing point of water and below that of the freezing point of pure acetic acid, 16.7° C. The water may then be removed by pouring it from the solid acetic acid. Because of its property of freezing, pure acetic acid is also known as glacial acetic acid.

58. **Vinegar.**—When fermented liquids such as wine and cider that contain small quantities of alcohol are subjected to the combined actions of the oxygen of the air and certain bacteria called *mycoderma aceti*, the alcohol is converted into acetic acid. These bacteria are always present in the atmosphere, and in the presence of the nitrogenous and mineral substances found in weak wines and ciders, they multiply rapidly. Strong solutions of alcohol kill these bacteria.

Two well-known processes for the manufacture of vinegar are the French, or Orleans, process, and the quick, or German, process. In the French process it is made by placing warm vinegar in large vats that have already been used for the operation and are impregnated with the peculiar vinegar ferment, and wine is then added. In about two weeks the fermentation is complete and a portion of the vinegar is withdrawn and replaced by a new quantity of wine, which also becomes converted into vinegar.

In the quick, or German, method of making vinegar, alcohol of strength of 6 to 10 per cent, is allowed to drop slowly, from a perforated shelf, into a quantity of beechwood shavings contained in a vat with a perforated false bottom. The shavings are previously soaked in vinegar to impregnate them with the *mycoderm*, or acetic ferment. Holes are bored in the side of the vat near the bottom to admit an ascending stream of air passing in a direction opposite to that of the alcohol. The shavings distribute the liquid over a very large surface, thus aiding the oxidizing action of the air, while at the same time they serve as a feeding ground for the bacteria. The mixture is passed through the barrel three or four times, and the conversion into vinegar is complete in about 36 hours. If the supply of air is insufficient, alcohol is lost in the form of acetaldehyde, the odor of which pervades the air.

White vinegar is prepared from light wines, while malt vinegar is prepared from an infusion of malt. Vinegar contains from 4 to 8 per cent. of acetic acid, and upon distillation a weak acetic acid is obtained.

59. Properties of Acetic Acid.—Anhydrous, or glacial, acetic acid is a solid below 16.7° C., closely resembling ice. Above this temperature it is a strongly acid liquid, with a penetrating odor. It has a specific gravity of 1.058 at 15° C. and boils at 118° C. Its vapor is inflammable, burning with a blue flame. Acetic acid is an excellent solvent for organic compounds. It mixes with water and alcohol in all proportions. The pure substance acts upon the skin in the same manner as formic acid.

Acetic acid in the dilute, impure form known as *vinegar*, is used extensively for pickles and spices. It is used in the dye industry and in calico printing in the form of iron and aluminum salts, these salts forming insoluble basic compounds in the fabric, known as *mordants*.

Acetic acid forms two classes of derivatives: Those that have lost their acid properties and are derived by the replacement of the acid hydrogen; and those that retain the acid properties, being derived by the replacement of the hydrogen of the hydrocarbon radical.

60. Inorganic Salts of Acetic Acid.—The salts of acetic acid are known as acetates. Most of them are soluble in water. The preparation and properties of only a few of the commoner salts are given.

Potassium acetate, CH_3COOK, is prepared by saturating acetic acid with potassium carbonate and evaporating the solution to dryness. It is a white, crystalline, hygroscopic powder, with a saline taste, is very soluble in water, and melts at 292° C.

Sodium acetate, $CH_3 \cdot COONa \cdot 3H_2O$, is prepared in the same way as the potassium salt. It crystallizes in colorless, monoclinic crystals, that effloresce on exposure to air, melt at 58° C., and are very soluble in water.

Lead acetate, $(CH_3 \cdot COO)_2Pb \cdot 3H_2O$, which is commonly known as *sugar of lead*, is made by dissolving lead oxide in acetic acid. It crystallizes in colorless, translucent crystals, is soluble in 1.5 parts of water at 15° C., has a sweet, metallic taste, is poisonous, and loses its water of crystallization at 75° C. It boils at 280° C.

Copper acetate, $(CH_3COO)_2Cu \cdot H_2O$, is prepared by dissolving copper hydroxide or carbonate in acetic acid. It forms beautiful bluish-green crystals, which dissolve in five times their weight of water. It has a metallic taste and an acetic acid odor. It melts at 240° C., undergoing decomposition.

Basic copper acetate, $CuO \cdot (CH_3COO)_2Cu \cdot 6H_2O$, or *verdigris*, is formed by exposing sheets of copper to the action of acetic acid in the air. The sheets of copper are piled up in layers with grape pulp. The sugar in the pulp ferments, and the alcohol thus formed is oxidized by the oxygen of the air to acetic acid. Verdigris comes into the market in the form of a very fine, greenish-blue powder. It is soluble in water and is used chiefly in the manufacture of pigments.

The acetate of copper and arsenic, $3CuO \cdot As_2O_3 \cdot (CH_3COO)_2Cu$, variously known as *emerald green*, *Schweinfurth*, *imperial*, and *Paris green* is *cupric aceto-arsenite* and is made by boiling verdigris with arsenic trioxide. As its name implies, it is an emerald green powder and, notwithstanding its poisonous character, is used as a coloring pigment for wall-papers, etc.

Ferric acetate, $(CH_3 \cdot COO)_3Fe$, is formed by adding sodium acetate to an acidified solution of a ferric salt. The solution at first is blood-red, but, upon boiling, the iron is precipitated as the hydroxide. Ferric acetate forms brownish-red scales that are soluble in water, and it is used in the arts and as a tonic.

Ferrous acetate, $(CH_3 \cdot COO)_2Fe$, under the name of *iron liquor*, is largely used as a mordant in dyeing. It is formed by the action of acetic acid on metallic iron.

HALOGEN DERIVATIVES OF ACETIC ACID

61. Acetyl Chloride, CH_3COCl.—When an alcohol is treated with phosphorus trichloride, the hydroxyl group is replaced with chlorine. If acetic acid is thus treated, the same reaction takes place, forming *acetyl chloride*, $CH_3 \cdot COCl$. This compound was discovered by Gerhardt in 1852 and is made by distilling acetic acid with phosphorus trichloride. The reaction is represented as follows:

$$3CH_3 \cdot COOH + PCl_3 = 3CH_3 \cdot COCl + P(OH)_3$$

Acetyl chloride is a colorless, highly refractive liquid that has a specific gravity of 1.131 at 0° C. and boils at 50.9° C. It has a very irritating odor, fumes in the air, and reacts violently with water, decomposing into acetic and hydrochloric acids. It is used as a reagent in detecting the presence of the hydroxyl group in organic compounds. When an alcohol is treated with acetyl chloride, the CH_3CO group of the latter replaces the hydrogen atom of the hydroxyl group, forming an ethereal salt, as is shown by the equation

$$CH_3 \cdot OH + CH_3 \cdot COCl = CH_3 \cdot COOCH_3 + HCl$$

62. Acetyl Bromide, $CH_3 \cdot COBr$, and Acetyl Iodide, $CH_3 \cdot COI$.—Acetyl bromide and acetyl iodide are the reaction products of acetic acid with phosphorus pentabromide, and acetic acid with phosphorus and iodine. The bromide is a colorless, fuming liquid that turns yellow in the air, boils at 81° C., and has an irritating odor. It is used as a reagent in organic synthesis and analysis; it also reacts violently with water. The iodide is a brown, transparent, fuming liquid, has a specific gravity of 1.98 at 17° C., and boils at 108° C.

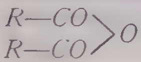
63. Halogen Acetic Acids.—The halogen substitution products of acetic acid bear the same relation to acetic acid as the substitution products of methane bear to methane. They are formed by the substitution of halogen atoms for the hydrogen of the hydrocarbon radical and are acid in their properties. The best known of these products are the chlorine compounds: *monochloracetic acid*, $CH_2 \cdot Cl \cdot COOH$, *dichloracetic acid*, $CH \cdot Cl_2 \cdot COOH$, and *trichloracetic acid*, $C \cdot Cl_3 \cdot COOH$.

Monochloracetic acid, $CH_2 \cdot Cl \cdot COOH$, is obtained by passing chlorine into boiling acetic acid containing sulphur or iodine. It is a very deliquescent, colorless, crystalline solid and has a specific gravity of 1.366 at 73° C. It melts at 63° C., boils at 186° C., and is soluble in water.

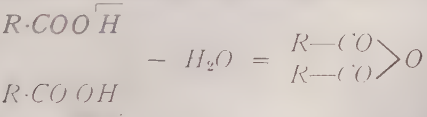
Dichloracetic acid, $CH\cdot Cl_2\cdot COOH$, is best prepared from chloral by treatment with potassium cyanide. It is a colorless liquid having a specific gravity of 1.572 at 13° C., is soluble in water and alcohol, and boils at 190° C.

Trichloracetic acid, $C\cdot Cl_3\cdot COOH$, can be prepared by the action of chlorine and sunlight upon glacial acetic acid. It is best prepared by the oxidation of chloral, and is a deliquescent, colorless, crystalline solid, with a pungent, suffocating odor. It is freely soluble in water, alcohol, and ether, melts at 57.3° C., and boils at 195° C. Trichloracetic acid is very unstable, decomposing on boiling with water into chloroform and carbon dioxide.

ACID ANHYDRIDES



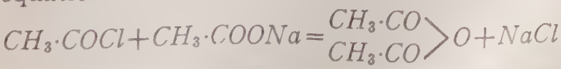
64. General Formula.—Acid anhydrides have the general formula $\left.\begin{matrix}R—CO\\R—CO\end{matrix}\right>O$ in which R represents any alkyl radical. They may be regarded as being formed by the elimination of one molecule of water from two molecules of the acid. Thus,



$$\begin{matrix}R\cdot COO\,H\\ \\ R\cdot CO\,OH\end{matrix} - H_2O = \left.\begin{matrix}R—CO\\R—CO\end{matrix}\right>O$$

It is not possible, however, to prepare all of them by treating the acid with dehydrating agents. Acid anhydrides react readily with water to reform the acids from which they have been derived. They are used in detecting the presence of the hydroxyl group in organic compounds.

65. Acetic Anhydride, $(CH_3\cdot CO)_2O$.—Acetic anhydride, also known as diacetyl oxide, is made by heating acetyl chloride with sodium acetate. This method is typical, as all of the anhydrides of the fatty acids may be made in a similar manner. In this case the reaction that takes place may be represented by the equation



$$CH_3\cdot COCl + CH_3\cdot COONa = \left.\begin{matrix}CH_3\cdot CO\\CH_3\cdot CO\end{matrix}\right>O + NaCl$$

Acetic anhydride is a colorless and strongly refractive liquid, with a strong acetic odor, and irritates the eyes. It boils at

139.5° C. and has a specific gravity of 1.08 at 15° C. It is soluble in about ten parts of water, at ordinary temperatures, with the slow formation of acetic acid. It differs in this respect from acetyl chloride, which reacts rapidly and vigorously with water, yielding acetic acid and hydrochloric acid. It is used in testing for the presence of the hydroxyl group.

PROPIONIC ACID

66. Preparation.—Propionic acid, C_2H_5COOH, is formed in small quantity when wood is subjected to destructive distillation. It is also formed by the fermentation of calcium lactate and tartrate. It may be obtained by treating ethyl cyanide, C_2H_5CN, with caustic potash, thus:

$$C_2H_5CN+KOH+H_2O=C_2H_5COOK+NH_3$$

The potassium propionate formed is then treated with dilute sulphuric acid, propionic acid being set free, thus:

$$C_2H_5COOK+H_2SO_4=C_2H_5COOH+KHSO_4$$

Propionic acid is most readily obtained, however, by oxidizing propyl alcohol with potassium dichromate and sulphuric acid.

67. Properties.—Propionic acid is a clear, colorless liquid with a penetrating odor similar to that of acetic acid. It has a specific gravity of 1.013, boils at 141° C., and is miscible in all proportions with water. It is the first acid that approaches the higher fatty acids in its behavior. It also yields a large number of derivatives corresponding to those of acetic acid.

Although propionic acid is a monobasic acid, it is capable of forming two isomeric compounds besides the one formed with metals. The difference between these two series of derivatives is due to different relations between the constituents. The possibility of these two isomeric acids is shown by the structural formula, namely, $CH_3{\cdot}CH_2{\cdot}COOH$. When the hydrogen of the CH_2 group is replaced by chlorine, a compound of the formula $CH_3{\cdot}CHCl{\cdot}COOH$, or chlorpropionic acid is obtained. When chlorine replaces the hydrogen of the CH_3 group another chlorpropionic acid is obtained having the formula $CH_2Cl \cdot CH_2 \cdot COOH$. One of these is known as **α-chlorpropionic acid*, and the other as *β-chlorpropionic acid*. Which of these substitution products is the α-acid and which is the β-acid can be determined only by carefully studying all the reactions and the methods of formation of both compounds. When the hydroxyl of lactic acid is replaced by chlorine, α-chlorpropionic acid is obtained; and when α-chlorpropionic acid is treated with caustic potash, lactic acid is obtained. Inasmuch as the structure of lactic acid is represented by the formula $CH_3 \cdot CH(OH) \cdot COOH$, the general formula for an α-product must be $CH_3 \cdot CHX \cdot COOH$, and further the general formula for a β-product must be $CH_2X \cdot CH_2 \cdot COOH$, in which X is any univalent group or atom. By continuing this line of reasoning it will be found that any monosubstitution product of propionic acid that can be obtained directly from α-chlorpropionic acid or that can be directly converted into this acid must be an α-product.

HIGHER FATTY ACIDS

68. Importance.—Those fatty acids of the paraffin series following acetic and up to palmitic acid are comparatively of so little importance that they will not be described. Suffice it to say that all of them occur naturally and can be prepared in the laboratory by methods analogous to those used in the preparation of formic acid. Palmitic and stearic acids are of interest, however, because they are contained in all ordinary soaps.

69. Palmitic Acid, $C_{15}H_{31}COOH$.—Palmitic acid is obtained as the result of the saponification of fats with alkalies, acids, or steam. It is prepared on a commercial scale by the saponification of spermaceti. The process is carried out by heating the spermaceti either with slaked lime or with concentrated sulphuric acid. When sulphuric acid is used, a slight carbonization takes place, imparting a dark color to the fatty acid. This can be removed by distilling the latter with superheated steam. In the laboratory palmitic acid is obtained by heating palm oil with an alcoholic solution of caustic potash. In this method a mixture of potassium palmitate and oleate is obtained, and a mixture of the acids is set free by means of dilute sulphuric acid. The mixed acids are washed free from sulphuric acid, dried and are then dissolved in hot alcohol from which the palmitic acid crystallizes out on cooling, leaving the oleic acid in solution.

---

*The Greek letters commonly used in naming certain types of organic compounds are the first four letters of the Greek alphabet, namely, *α, alpha, β, beta, γ, gamma*, and *δ, delta*. In the case of the halogen substituted propionic acids, the carbon atom connected to the carboxyl group is the alpha carbon atom.

Palmitic acid is a white, tasteless, crystalline solid that melts at 60° C. At a higher temperature it takes fire and burns with a bright but somewhat smoky, flame. It is insoluble in water but readily soluble in hot alcohol and ether from which solution it crystallizes in the form of needles on cooling. When animal bodies decompose in the earth, a wax-like mass composed of a mixture of calcium and potassium palmitates, is left.

70. Stearic Acid, $C_{17}H_{35}COOH$.—Stearic acid, mixed with oleic and palmitic acids, occurs in animal fats and tallows. The acids are set free by the methods used for the preparation of palmitic acid. After washing and drying, they are dissolved in the least necessary quantity of hot alcohol. In this way oleic acid is retained in solution and a mixture of stearic and palmitic acids is deposited on cooling the solution. Stearic acid may be separated from the palmitic acid by a fractional crystallization from alcohol. Palmitic acid is more soluble in alcohol than is stearic acid, and after each crystallization, the crystals contain less and less palmitic acid. The operation is continued until a product melting at 69° C. or higher is obtained.

71. Pure stearic acid is usually obtained as a solid, white, crystalline mass. It is odorless and tasteless, melts at 69.32° C., and, under a pressure of 100 millimeters, boils at 287° C. Its specific gravity is 1, thus equaling that of water. It is insoluble in water, but dissolves readily in boiling alcohol or ether. It is inflammable and burns with a bright luminous flame. Stearic acid dissolves in the alkalies on heating, forming stearates, which are the components of ordinary soap. Sodium and potassium stearates are soluble in water, but the other stearates are insoluble. Calcium and magnesium stearates are precipitated when hard water is brought in contact with a soap solution.

Impure stearic acid is used in the manufacture of the so-called stearin candles. The fat is saponified and yields a mixture of palmitic and stearic acids and liquid oleic acid that is semisolid at ordinary temperatures. This mixture, is pressed, first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids. The solid white stearin thus obtained is melted, a small proportion of paraffin wax added to prevent crystallization of the fatty acids, which would make the candles brittle, and the melted substance poured into molds, in the center of which wicks are fastened.

SOAPS

72. When fats are heated with aqueous solutions of alkalies, saponification occurs and the alkali salts of the fatty acids are formed; these salts are called *soaps*. Thus, it is seen that soaps are the alkali-metal salts of acids contained in fats. Soap made by boiling the fat with caustic potash is usually yellow and is known as *soft soap*; the hard soaps are those made with caustic soda and are in solution after saponification is complete. They are separated from the reaction mixture by adding sodium chloride, or common salt. This process is commonly called *salting out*. Another difference between the soft and hard soaps is that the soft soaps contain not only the potassium salts of the acids, but also the glycerol produced, and a considerable proportion of water. The hard soaps, on the other hand, consist of the sodium salts of the acids, with only a small quantity of water, the glycerol remaining in the brine resulting from the salting out.

ETHEREAL SALTS, OR ESTERS

PROPERTIES AND FORMATION

73. General Properties.—When an acid acts on the hydroxide of a metal, a salt and water are formed. In the same manner, when an acid acts on an alcohol, the acid is either wholly or partly neutralized, with the formation of an ethereal salt. The word *salt* is rather misleading in this case, as, like alcohol, the lower ethereal salts, or esters, are liquids volatilizing without decomposition, and many are volatile at the ordinary temperature. The ethereal salts of the higher fatty acids are solids. They are lighter than water, and many of them are characterized by a pleasant odor and taste. They are frequently used in soaps, syrups, jellies, flavoring extracts, and perfumery.

The odor of flowers and the taste of fruits are due to the presence of esters. Great deception is practiced by offering esters as pure fruit juices. Some of the most common are: oil of wintergreen, *methyl salicylate*, $C_6H_4 \cdot OH \cdot COOCH_3$; essence of pineapples, *ethyl butyrate*, $C_3H_7COOC_2H_5$; essence of apples, *amyl valerate*, $C_4H_9 \cdot COOC_5H_{11}$, and essence of banana, *amyl acetate*, $CH_3COOC_5H_{11}$.

74. Formation of Esters.—The following methods are commonly used in the preparation of esters:

1. By the direct union of an alcohol and an acid. This method is limited to a few of the strongest acids, thus:

$$CH_3 \cdot OH + HNO_3 = CH_3 \cdot NO_3 + H_2O$$

2. By treating an acid chloride with an alcohol, as is shown by the equation

$$CH_3 \cdot COCl + CH_3 \cdot OH = CH_3 \cdot COOCH_3 + HCl$$

3. By the treatment of the silver salt of the acid with a halogen substitution product of a hydrocarbon. This reaction is

$$CH_3 \cdot COOAg + CH_3 \cdot Cl = CH_3 \cdot COOCH_3 + AgCl$$

ESTERS OF INORGANIC ACIDS

75. Methyl Sulphuric Acid, $CH_3 \cdot HSO_4$.—To prepare methyl sulphuric acid, or *methyl hydrogen sulphate*, methyl alcohol is carefully mixed with double its quantity, by weight, of concentrated sulphuric acid and is then heated until the mixture boils. After cooling, the mixture is diluted with water and neutralized with barium carbonate, thus removing the free sulphuric acid as barium sulphate and leaving barium sulphomethylate in solution. The solution is filtered and evaporated, when the barium salt crystallizes in square, colorless crystals of the composition $Ba(CH_3SO_4)_2 \cdot 2H_2O$. These crystals are dissolved in water, the barium precipitated with sulphuric acid, and the solution allowed to evaporate to a syrupy liquid. Methyl sulphuric acid is very unstable, but, together with its salts, is very soluble in water.

76. Methyl Sulphate, $(CH_3)_2SO_4$.—Methyl sulphate, also known as dimethyl sulphate, is prepared by the vacuum distillation of methyl sulphuric acid and subsequent purification by distillation with powdered anhydrous barium oxide. The reaction is shown by the equation

$$2CH_3 \cdot HSO_4 = (CH_3)_2SO_4 + H_2SO_4$$

Methyl sulphate is a colorless, oily liquid, with an odor resembling that of garlic. It has a specific gravity of 1.32 and boils at 188° C. It is neutral to test paper and is not soluble in water, being decomposed by it. Many of its reactions are those of inorganic salts. Treated with sodium chloride, it yields methyl chloride and sodium sulphate, thus:

$$(CH_3)_2SO_4 + 2NaCl = 2CH_3Cl + Na_2SO_4$$

Methyl sulphate is often used to introduce methyl groups into organic compounds.

77. Methyl Nitrate, CH_3NO_3.—Methyl nitrate is obtained by treating equal parts by weight of potassium nitrate and methyl alcohol with twice the quantity of sulphuric acid. The heat produced by the reaction is sufficient to distil the methyl nitrate. It is a colorless liquid with a specific gravity of 1.216 at 15° C., and boils at 65° C., at which temperature it also explodes. Methyl nitrate can be made with some difficulty by the direct action of nitric acid upon methyl alcohol.

78. Ethyl Sulphuric Acid, $C_2H_5HSO_4$.—The preparation of ethyl sulphuric acid is accomplished by means of the same method used for the preparation of methyl sulphuric acid. The acid salt is separated from the excess sulphuric acid by barium and the barium is then removed with the calculated amount of sulphuric acid. It is a colorless, oily liquid, having a specific gravity of 1.316 at 16° C., and dissolves in water and alcohol. Boiled with water it decomposes, yielding alcohol and sulphuric acid; this is shown by the equation

$$C_2H_5 \cdot HSO_4 + H_2O = C_2H_5 \cdot OH + H_2SO_4$$

All the salts of ethyl sulphuric acid are soluble in water, and crystallize readily.

79. Ethyl Sulphate, $(C_2H_5)_2SO_4$.—In the preparation of ethyl sulphate, ethyl sulphuric acid is distilled as in the case of methyl sulphate. It is also prepared by the third general method of preparation of esters, according to the following reaction:

$$Ag_2SO_4 + 2C_2H_5I = (C_2H_5)_2SO_4 + 2AgI$$

Ethyl sulphate is a colorless liquid having a specific gravity of 1.185 at 15° C.; it boils at 208° C. without decomposition. It is soluble in alcohol and ether but is insoluble in water; when heated with water, ethyl sulphate decomposes into alcohol and ethyl sulphuric acid.

80. Ethyl Nitrate, $C_2H_5NO_3$.—When nitric acid and ethyl alcohol are mixed and the mixture distilled, ethyl nitrate is formed. Care must be taken in its preparation as the presence of nitrous acid in the nitric acid used will cause a violent explosion, due to the nitrous acid oxidizing the alcohol to acetaldehyde and other products which react violently with the nitric acid. This is overcome by heating the nitric acid on a steam bath with urea, $CO(NH_2)_2$. After treatment the acid is cooled, more urea is added, then alcohol, and the mixture is distilled. The ethyl nitrate is separated from the alcohol in the distillate by being shaken with water and the addition of a little potassium hydroxide, the lower layer separated, allowed to stand over calcium chloride, and distilled. The nitrous acid is decomposed by the urea according to the reaction

$$2HNO_2+CO(NH_2)_2=CO_2+2N_2+3H_2O$$

Ethyl nitrate is a colorless, inflammable liquid, burning with a white flame. It has a pleasant odor and sweet taste, its specific gravity is 1.12 at 15° C., it boils at 87.6° C., and is soluble in alcohol and ether. It is almost insoluble in water and will explode if suddenly exposed to a high temperature.

81. Ethyl Nitrite, $C_2H_5NO_2$.—Pure ethyl nitrite is obtained when a mixture of ethyl alcohol and dilute sulphuric acid is added to a solution of potassium nitrite. The ethyl nitrite formed is caused to distil by the heat of the reaction and is condensed and collected in a receiver packed in ice.

Ethyl nitrite is a yellowish, highly aromatic, ethereal liquid, is exceedingly volatile, and very inflammable. Its specific gravity is .900 at 15° C., and it boils at 16.4° C. Its principal use is in medicine in the form of an alcoholic solution, containing not less than 4 per cent. of ethyl nitrite. This solution is the sweet spirits of niter. It is insoluble in water, and is gradually decomposed by it.

Ethyl nitrite can also be prepared by treating silver nitrite with ethyl iodide, thus:

$$C_2H_5I+AgNO_2=C_2H_5NO_2+AgI$$

When this reaction occurs two compounds are formed, both with the same empirical formula. But as they have widely different boiling points, they are easily separated by fractional distillation, one compound boiling at 114° C., while the ethyl nitrite boils at 16.4° C.

ESTERS OF ORGANIC ACIDS

82. Methyl Formate, $H\cdot COOCH_3$.—Methyl formate may be prepared by distilling methyl alcohol with sodium formate and hydrochloric acid, or by heating a mixture composed of equal parts of potassium methyl sulphate and sodium formate, thus:

$$H\cdot COONa+CH_3KSO_4=H\cdot COOCH_3+KNaSO_4$$

The formula for methyl formate indicates that it is an isomeride of acetic acid. It is soluble in alcohol, boils at 31.7° C., and has a specific gravity of .9797 at 15° C.

83. Methyl Acetate, $CH_3{\cdot}COOCH_3$.—When wood is destructively distilled, methyl acetate is one of the products formed. It is prepared by distilling a mixture consisting of 1 part of glacial acetic acid, 1 part of sulphuric acid, and 2 parts of methyl alcohol. It is a colorless, fragrant liquid, is soluble in all proportions of water, boils at 54° C., and has a specific gravity of .924 at 20° C.

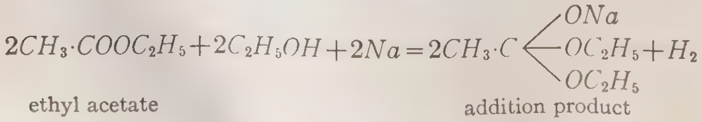
84. Ethyl Formate, $H{\cdot}COOC_2H_5$.—Ethyl formate results when a mixture consisting of alcohol, sodium formate, and sulphuric acid is distilled. It is a colorless liquid having an odor resembling that of peach kernels. It has a specific gravity of .917 at 15° C. and boils at 54° C. It is soluble in water but decomposes on long standing. It is isomeric with methyl acetate and propionic acid.

85. Ethyl Acetate, $CH_3{\cdot}COOC_2H_5$.—Ethyl acetate is obtained by distilling a mixture of alcohol, sulphuric acid, and potassium acetate. The reaction is

$$\begin{aligned} &C_2H_5{\cdot}OH+H_2SO_4+CH_3{\cdot}COOK \\ &=CH_3{\cdot}COOC_2H_5+KHSO_4+H_2O \end{aligned}$$

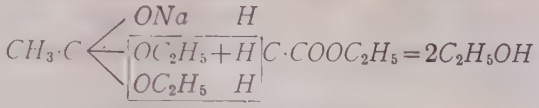
It is a colorless liquid with an odor like cider, and has a specific gravity of .925 at 0° C., boils at 77° C., and is soluble in water. It is miscible in all proportions with alcohol and ether.

86. Ethyl Aceto Acetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COO{\cdot}C_2H_5$.—Ethyl aceto acetate, also known as aceto acetic ether, is obtained by by the action of metallic sodium on ethyl acetate in the presence of ethyl alcohol. The reactions that take place are complicated. They are represented by the following equations:



$$2CH_3{\cdot}COOC_2H_5+2C_2H_5OH+2Na=2CH_3{\cdot}C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases}+H_2$$

The addition product thus formed reacts with another molecule of ethyl acetate, according to the equation



$$CH_3\cdot C\left\langle\begin{array}{ll} ONa & H \\ OC_2H_5+ & H \\ OC_2H_5 & H \end{array}\right. C\cdot COOC_2H_5=2C_2H_5OH$$

$$+CH_3\cdot CONa\cdot CH\cdot COOC_2H_5$$

ethyl sodio aceto acetate

and ethyl sodio aceto acetate reacts with acetic acid to form ethyl aceto acetate, thus:

$$CH_3\cdot CONa\cdot CH\cdot COOC_2H_5+CH_3COOH$$
$$=CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5+CH_3\cdot COONa$$

ethyl aceto acetate

87. Ethyl aceto acetate is a colorless liquid that has a specific gravity of 1.03 at 15° C., and boils at 181° C. It has an agreeable odor and is slightly soluble in water. It is soluble in alcohol, its alcoholic solution giving a violet color with ferric chloride and a green crystalline precipitate with a strong solution of copper acetate. It is of inestimable value in synthetic organic chemistry, for through its use a large number of complex compounds have been made, because when ethyl aceto acetate is heated with dilute sulphuric acid, or with a dilute aqueous solution of an alkali, a ketone is obtained. On the other hand, when treated with a concentrated alcoholic solution of caustic potash or caustic soda, an acid decomposition takes place. If the sodium in ethyl sodio aceto acetate is replaced by a radical the compound $CH_3\cdot CO\cdot CHR\cdot COO\cdot C_2H_5$ is obtained; and if this is subjected to the ketone decomposition, $CH_3\cdot CO\cdot CH_2R$ is obtained, and by the acid reaction it is possible to obtain $CH_2R\cdot COOH$. But as sodium can again react with the compound $CH_3\cdot CO\cdot CHR\cdot COOC_2H_5$ to replace hydrogen, $CH_3\cdot CO\cdot CRR'\cdot COOC_2H_5$ will be formed; and this by the ketone and acid decompositions yield $CH_3\cdot CO\cdot CHRR'$ and $CHRR'\cdot COOH$, respectively.

HYDROLYSIS AND SAPONIFICATION

88. When an ester is heated with water, it decomposes with the formation of the alcohol and the acid from which it was originally prepared, thus:

$$CH_3{\cdot}COOC_2H_5+H_2O=C_2H_5OH+CH_3{\cdot}COOH$$

The decomposition is never complete, however, since when the concentrations of the alcohol and acid in the mixture reach a certain point, they tend to recombine with the formation of the ester. This, then, is an example of a reversible reaction. In the reaction given, ethyl acetate has been broken up to form the compounds ethyl alcohol and acetic acid, and, since the decomposition was caused by the action of water, the ester is said to have been *hydrolyzed.* Hydrolysis is then the decomposition of one compound into two or more compounds, the elements of water being taken up in the process. Additional examples of hydrolysis that will be treated more fully in another Section are as follows:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}}+H_2O=\underset{\text{glucose}}{C_6H_{12}O_6}+\underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{methyl cyanide}}{CH_3{\cdot}CN}+2H_2O=CH_3{\cdot}COOH+NH_3$$

The hydrolysis of an ester may be much more rapidly accomplished by the action of acids and caustic alkalies. When the latter are used, the resulting hydrolysis yields the alcohol and a salt of the acid, thus:

$$CH_3{\cdot}COOC_2H_5+NaOH=C_2H_5OH+CH_3{\cdot}COONa$$

An hydrolysis of this kind is termed *saponification* because reaction is the same as that which takes place in the preparation of soaps. In the case of hydrolysis by mineral acids, the function of the latter is merely that of a catalytic agent.

ETHERS

89. Structure of Ethers.—When metallic sodium reacts with ethyl alcohol, sodium ethylate, C_2H_5ONa, is formed, and when this compound reacts with an alkyl halide, a compound known as an *ether* is obtained, thus:

$$C_2H_5ONa+C_2H_5I=C_2H_5\cdot OC_2H_5+NaI$$

The same compound is also formed when dry silver oxide, Ag_2O, reacts with ethyl iodide, according to the equation

$$2C_2H_5I+Ag_2O=(C_2H_5)_2O+2AgI$$

These reactions are typical of the formation of the ethers and indicate that they are the oxides of alkyl radicals. From the methods of formation given, it is obvious that ethers composed of unlike radicals linked to oxygen can also be prepared. Thus, when sodium ethylate and methyl iodide are brought together, an ether having the composition $C_2H_5\cdot O\cdot CH_3$ is obtained. Ethers are of this type are designated as *mixed ethers*. These methods merely serve to show the structure of an ether. The methods by which ethers are prepared in the laboratory and on a large scale are entirely different.

90. Methyl Ether, $CH_3\cdot O\cdot CH_3$.—Methyl ether may be made by heating a mixture of methyl alcohol and sulphuric acid. As it is formed, the ether passes over as a colorless gas and is collected over mercury. It is condensed at a low temperature and under pressure to a liquid having a specific gravity of 1.617 and boiling at $-23.6°$ C. It has an ethereal odor, burns with a pale flame, and is soluble in alcohol, wood spirits, and sulphuric acid. Cold water dissolves about 40 times its volume of methyl ether, acquiring its characteristic taste and odor. On boiling the solution, the gas is liberated.

91. Ethyl Ether, $C_2H_5\cdot O\cdot C_2H_5$.—The best-known ether of the series is ethyl ether, which is variously known under the names of diethyl ether, sulphuric ether, or simply ether. It is prepared in the laboratory and manufactured on a large scale by heating a mixture of ethyl alcohol and sulphuric acid. In carrying out the process, molecular proportions of alcohol and acid are used; that is, 46 grams of alcohol for every 98 grams of sulphuric acid. The acid is added to the alcohol in a flask, in small quantities at a time, and the contents of the flask stirred and cooled after each addition. When all of the acid has been added and the mixture cooled to room temperature, the flask is fitted with a dropping funnel and is connected with a condenser. The reaction mixture is then heated to 140° C. and alcohol added by means of the dropping funnel, the stem of which passes below the surface of the reaction mixture. A thermometer, the bulb of which passes into the reaction mixture, indicates the temperature. The alcohol is added at such a rate that the liquid in the flask is always at approximately the same level. As the fresh alcohol is introduced, a mixture of ether, water containing sulphur dioxide, and alcohol collects in the receiver and separates into two layers, the upper one being the ether. The entire distillate is placed in a separatory funnel, and a separation of the ether layer from the water layer is effected. The ether is then shaken with cold water, which removes most of the alcohol. After separating again, the product still contains some water, alcohol, and sulphur dioxide. The last is removed by shaking the ether with a dilute solution of sodium carbonate. When this has been separated, the ether is dried over anhydrous calcium chloride or over lime. It is then distilled over a water bath. The ether thus obtained contains traces of water and alcohol that may be removed by allowing it to stand over thin bright shavings of metallic sodium, sodium ethylate and sodium hydroxide being formed. On redistilling, pure ether is obtained.

92. While the foregoing process of manufacturing ether is known as the continuous etherification process it is only continuous in a limited sense. After about six times the original quantity of alcohol has been added, the distillate becomes richer and richer in alcohol and water, until finally ether is no longer formed. This process for the manufacture of ether is explained as follows: When the alcohol and the sulphuric acid are brought together ethyl sulphuric acid is formed, the reaction being

$$C_2H_5OH + H_2SO_4 = C_2H_5 \cdot HSO_4 + H_2O$$

When the ethyl sulphuric acid is heated with alcohol, ether is formed, and the sulphuric acid is regenerated. This is shown by the equation

$$C_2H_5{\cdot}HSO_4+C_2H_5{\cdot}OH=C_2H_5{\cdot}O{\cdot}C_2H_5+H_2SO_4$$

In the formation of ethyl sulphuric acid from alcohol and sulphuric acid, water is obtained as a by-product. Upon distilling the ether formed, part of the water passes over with the ether and part remains. The part that remains decomposes the ethyl sulphuric acid, as it is formed, into alcohol and sulphuric acid, thus:

$$C_2H_5{\cdot}HSO_4+H_2O=C_2H_5{\cdot}OH+H_2SO_4$$

Hence, when the amount of water in the flask reaches a certain limit, it stops the production of ether by preventing the formation of the ethyl sulphuric acid.

93. Properties of Ethyl Ether.—Ether is a clear, colorless liquid with a pleasant characteristic odor, and a burning, sweetish taste. It has a specific gravity .7199 at 15° C., and boils at 35° C. It may be frozen to a solid that melts at −116° C. It is slightly soluble in water, one volume dissolving in ten volumes of water at 25° C., and water is slightly soluble in ether. Ether is soluble in alcohol, chloroform, and benzene. It is extremely volatile and its vapor is highly inflammable, burning with a luminous flame. When the vapor of ether is mixed with air, it forms an extremely explosive mixture. When dropped on the hand, it produces the sensation of cold, owing to its rapid vaporization. The vapor of ether, when inhaled, produces unconsciousness.

Heated to 150° C. in a sealed tube with water and an acid, hydrolysis takes place and it is converted into alcohol. This reaction is shown by the equation

$$C_2H_5{\cdot}O{\cdot}C_2H_5+H_2O=2C_2H_5{\cdot}OH$$

Treated with hydriodic acid gas at a low temperature, alcohol and ethyl iodide are formed, as is shown by the equation

$$C_2H_5{\cdot}O{\cdot}C_2H_5+HI=C_2H_5{\cdot}OH+C_2H_5I$$

Ether is used in the laboratory as a solvent for oils, fats, resins, etc. It is also used in the manufacture of collodion, smokeless powder and in many other processes.

94. Mixed Ethers.—When an alcohol other than ethyl alcohol is allowed to flow into a mixture of ethyl alcohol and sulphuric acid, a mixed ether is obtained. Thus, if methyl alcohol is used, methyl ethyl ether is obtained, the reaction being

$$CH_3OH+C_2H_5\cdot HSO_4=CH_3\cdot O\cdot C_2H_5+H_2SO_4$$

Mixed ethers have the same chemical and general properties as the simple ethers; however, if a mixed ether is treated with hydriodic acid the radical containing the most carbon is converted into an alcohol, thus:

$$CH_3\cdot O\cdot C_2H_5+HI=C_2H_5\cdot OH+CH_3I$$

SULPHUR DERIVATIVES

MERCAPTANS, OR SULPHUR ALCOHOLS

95. Structure.—The name *mercaptan* is taken from the Latin, *mercurium captans*, because of the property of these compounds of combining with mercuric oxide to form new compounds. The sulphur alcohols, as the name would indicate, have the same general structure as the primary alcohols previously studied, sulphur taking the place of oxygen in the molecule. Thus, the general formula for a primary alcohol of the aliphatic series may be written $R—OH$, while that for a sulphur alcohol is written $R—SH$.

96. General Methods of Preparation.—The sulphur derivatives are obtained by the action of a hydrosulphide, such as potassium hydrosulphide, KSH, on an alkyl alkali sulphate, such as methyl potassium sulphate, $CH_3\cdot KSO_4$, or by the action of phosphorus pentasulphide, P_2S_5, on an alcohol.

97. General Properties.—The mercaptans, like the alcohols, are volatile, but their boiling points are somewhat lower than those of the corresponding alcohols. They are insoluble in water but soluble in alcohol and ether; the higher members are crystallizable.

Alcohols do not form salts with the bases of the heavy metals, whereas mercaptans yield *mercaptides*, that have the general formula $R—S—M$, in which M represents a monovalent metal. In the case of a divalent metal the formula is $(R—S)_2M$. An alcohol which dissolves with difficulty in water does not dissolve in solutions of the alkalies; but the mercaptans, although insoluble in water, dissolve readily in solutions of the alkalies, forming mercaptides. Hence, they are of an acidic character. However, the mercaptans are liberated from all mercaptides by mineral acids. All the lower members have powerful, offensive, penetrating odors.

98. Methyl Mercaptan, $CH_3 \cdot SH$.—Methyl mercaptan is prepared by treating methyl potassium sulphate with potassium hydrosulphide. The reaction which takes place may be represented by the equation

$$CH_3 \cdot KSO_4 + KSH = CH_3 \cdot SH + K_2SO_4$$

It can also be prepared by the fermentation of albumen. It has an extremely disagreeable odor, and boils at 6° C.

99. Ethyl Mercaptan, $C_2H_5 \cdot SH$.—Ethyl mercaptan can be prepared by the methods used for the preparation of methyl mercaptan. It is also obtained by treating ethyl iodide with an alcoholic solution of potassium hydrosulphide. This substance is also known simply as *mercaptan*. It is a volatile liquid, and has a powerful odor resembling that of garlic. Its specific gravity is .835 and it boils at 36° C. It is inflammable, burning with a blue flame, and is slightly soluble in water but readily soluble in alcohol and ether..

Ethyl mercaptan is made on a large scale owing to its use in the manufacture of sulphonal, or diethylsulphonedimethylmethane.

100. Sulphonal, $(CH_3)_2 \cdot C \cdot (SO_2 \cdot C_2H_5)_2$.—When anhydrous acetone and ethyl mercaptan are brought together in the presence of dry hydrochloric-acid gas, water is eliminated in the reaction which takes place and dimethyldiethyl mercaptole is formed, thus:

$$(CH_3)_2 \cdot CO + 2C_2H_5 \cdot SH = (CH_3)_2 \cdot C \cdot (SC_2H_5)_2 + H_2O$$

When this compound is treated with potassium permanganate, its two sulphur atoms are oxidized and converted into

SO_2 groups with the formation of sulphonal, which is finally obtained in the form of a colorless crystalline powder. Sulphonal melts between 124° C., and 126° C. When heated to 300° C., it decomposes. It is used in medicine as a soporific, or sleep producer.

MERCAPTIDES

101. It has already been shown that the hydrogen atom of the hydroxyl group in an alcohol is replaceable by such metals as sodium and potassium. In the case of the sulphur alcohols. however, the hydrogen atom connected to sulphur is much more easily replaced, giving rise to many metallic mercaptides. Thus, sodium, potassium, mercury, lead, copper, and bismuth mercaptides are known. The reactions showing the formation of sodium and mercury mercaptides are represented as follows:

$$C_2H_5{\cdot}SH+Na=C_2H_5{\cdot}SNa+H$$
$$2C_2H_5{\cdot}SH+Hg=(C_2H_5{\cdot}S)_2Hg+2H$$

SULPHUR ETHERS

102. General Preparation and Properties.—A series of compounds that resemble the ethers, but that contain sulphur in the place of the oxygen of the ethers are the *sulphur ethers*, *thioethers*, or *alkyl sulphides*. These compounds are prepared by treating the halogen substitution products with potassium sulphide. The reaction that takes place then is shown by the equation

$$2RI+K_2S=R_2S+2KI$$

They can also be prepared by treating an alkyl alkali sulphate with a mercaptide, as is shown by the equation

$$R{\cdot}KSO_4+R{\cdot}SK=R_2S+K_2SO_4$$

The sulphur ethers bear the same relation to the mercaptans as the oxygen ethers bear to the oxygen alcohols. The sulphur ethers are liquids having a very disagreeable odor, are neutral compounds, and are insoluble in water. They yield double compounds with metallic salts.

103. Methyl Sulphide. $(CH_3)_2S$.—Methyl sulphide is made by treating a solution of potassium sulphide in methyl alcohol with methyl chloride. Methyl sulphide is a colorless liquid with a disagreeable odor, it boils at 38° C., has a specific gravity of .845 at 21° C., and is used as a solvent for anhydrous mineral salts.

104. Ethyl Sulphide, $(C_2H_5)_2S$.—Ethyl sulphide is obtained when ethyl potassium sulphate is treated with potassium sulphide; the reaction is as follows:

$$2C_2H_5 \cdot KSO_4 + K_2S = (C_2H_5)_2S + 2K_2SO_4$$

Ethyl sulphide is also made by treating the halogen derivative with potassium sulphide; in this case, the reaction is:

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI$$

If mercury mercaptide is distilled, ethyl sulphide or ethyl sulphur ether is obtained; this is shown by the equation

$$(C_2H_5S)_2Hg = (C_2H_5)_2S + HgS$$

Ethyl sulphide is a colorless oily liquid with an odor of garlic. It has a specific gravity of .8364, at 21° C., and a boiling point of 92° C. It is soluble in alcohol.

SULPHONIC ACIDS

105. When the mercaptans are oxidized, sulphonic acids are produced. These acids are isomeric with the esters of sulphurous acid, but differ from the organic sulphites in that when treated with a reducing agent they yield mercaptans. This reaction shows that since the sulphur in the mercaptans is linked directly to the carbon, the same must be true of the sulphonic acids. Therefore, the probable structure of ethyl sulphonic acid is $CH_3 \cdot CH_2 \cdot SO_3H$. When sulphonic acids are treated with phosphorus pentachloride, however, sulphonyl chlorides, $C_nH_{2n+1}SO_2Cl$ are obtained, hence the group SO_3H must contain hydroxyl and the structure must be $CH_3 \cdot CH_2 \cdot SO_2 \cdot OH$.

As the sulphonic acids contain one hydroxyl group, they are monobasic acids. They are hygroscopic, crystalline solids, and are very soluble in water, By means of a partial reduction, or by replacing the chlorine in the sulphonyl chlorides by nascent hydrogen, *sulphinic acids*, $C_nH_{2n+1}\cdot SO_2H$, are obtained.

Salts of the sulphonic acids can also be obtained by treating a halogen substitution product with an alkali sulphite, as is shown by the equation

$$RI+K_2SO_3=R\cdot SO_3K+KI$$

The sulphonic acids of the aliphatic series cannot be made by treating an aliphatic hydrocarbon or an alcohol with sulphuric acid.

ORGANIC CHEMISTRY
(PART 3)

DERIVATIVES OF SATURATED ALIPHATIC HYDROCARBONS

ALKYL COMPOUNDS OF NITROGEN

ALKYL AMINES OR SUBSTITUTED AMMONIAS

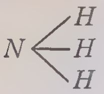
1. Structure of Amines.—It has been shown that the structure of any of the monohalogen substitution products of the saturated aliphatic hydrocarbons can be represented by the general formula, $C_nH_{2n+1}X$, in which X represents the halogen atom. The formula for methyl iodide is accordingly CH_3I, and when this compound is treated with alcoholic ammonia, hydriodic acid, and a compound having the empirical formula CH_5N, are obtained. Now, since methyl iodide contains but one atom of iodine and this is accounted for by the formation of hydriodic acid, it is evident that this acid is formed by the union of iodine with hydrogen from the ammonia. Thus, this reaction would leave the methyl radical and a residue NH_2, from the ammonia, free to combine and form the compound known as methyl amine, $CH_3 \cdot NH_2$. The reaction may be represented as follows:

$$CH_3I + NH_3 = CH_3 \cdot NH_2 + HI$$

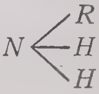
The NH_2 group is derived from ammonia by the removal of one hydrogen atom. For this reason it is called the *amino* radical.

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

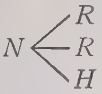
2. General Properties and Names.—The amines are either primary, secondary, or tertiary, depending on whether one, two, or three hydrogen atoms of ammonia have been replaced by an alkyl radical. This is graphically represented thus:



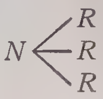
ammonia



primary amine

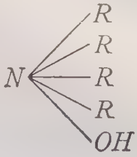


secondary amine



tertiary amine

3. Another compound, known as a *quaternary ammonium base* and corresponding to ammonium hydroxide, is also formed; it has the following composition:



The amines resemble ammonia very closely in their characteristics. The lower members, which are gases, are readily soluble in water, and possess a strong ammoniacal odor, but are distinguished from ammonia by their combustibility. The higher members are liquids, but they are also soluble in water. The very highest members are sparingly soluble in water; they are also odorless.

The amines unite directly with acids to form salts. Thus, when hydriodic acid is brought together with methyl amine, the compound $CH_3 \cdot NH_2 \cdot HI$, methyl ammonium iodide or methyl amine hydriodide is formed. When this salt is treated with sodium hydroxide, the amine is set free in the same manner as is ammonia when salts of the latter are treated with sodium hydroxide; thus,

$$CH_3 \cdot NH_2 + HI = CH_3 \cdot NH_2 \cdot HI$$
$$CH_3 \cdot NH_2 \cdot HI + NaOH = CH_3 \cdot NH_2 + NaI + H_2O$$

4. Preparation of Amines.—When a strong solution of ammonia in alcohol is heated with an alkyl iodide for some hours, at 100° C., in a closed flask, a primary, secondary, and tertiary amine, in the form of the hydriodide, and a tetra-alkyl-ammonium iodide are obtained. The following equations represent the successive steps of this formation when methyl iodide and ammonia are the compounds used:

$$CH_3{\cdot}I + NH_3 = CH_3{\cdot}NH_2{\cdot}HI$$

methyl ammonium iodide

$$CH_3{\cdot}NH_2{\cdot}HI + CH_3{\cdot}I = (CH_3)_2{\cdot}NH{\cdot}HI + HI$$

dimethyl ammonium iodide

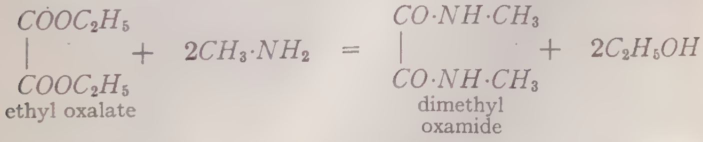
$$(CH_3)_2{\cdot}NH{\cdot}HI + CH_3{\cdot}I = (CH_3)_3{\cdot}N{\cdot}HI + HI$$

trimethyl ammonium iodide

$$(CH_3)_3{\cdot}N{\cdot}HI + CH_3{\cdot}I = (CH_3)_4{\cdot}N{\cdot}I + HI$$

tetramethyl ammonium iodide

After adding sodium-hydroxide solution to the mixture of amino salts formed, thus setting the amines free, the latter are distilled. The quaternary ammonium salt, in this case tetramethyl ammonium iodide, does not react with sodium hydroxide and does not distil. The mixture of mono-, di-, and trimethyl amines that collects in the receiver, which must be immersed in ice water, is now separated from the water that was distilled over with it, and a separation of the three amines effected as follows: Gaseous amines are passed into ethyl oxalate, $(C_2H_5)_2C_2O_4$, which is a liquid boiling at 186° C. When the amines are liquids, ethyl oxalate is merely added to them. In the case under discussion, methyl amine reacts with ethyl oxalate to form dimethyl oxamide, $(CO{\cdot}NH{\cdot}CH_3)_2$, which is a solid; thus,

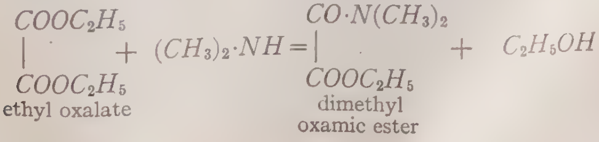


$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + 2CH_3{\cdot}NH_2 = \begin{array}{l} CO{\cdot}NH{\cdot}CH_3 \\ | \\ CO{\cdot}NH{\cdot}CH_3 \end{array} + 2C_2H_5OH$$

ethyl oxalate

dimethyl oxamide

The secondary compound reacts to form dimethyl oxamic ester, $(CO)_2{\cdot}O{\cdot}C_2H_5{\cdot}N(CH_3)_2$, which is a liquid. Thus,

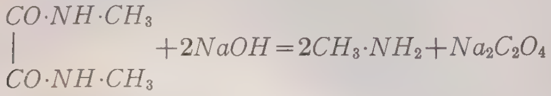


$$\begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} + (CH_3)_2{\cdot}NH = \begin{array}{l} CO{\cdot}N(CH_3)_2 \\ | \\ COOC_2H_5 \end{array} + C_2H_5OH$$

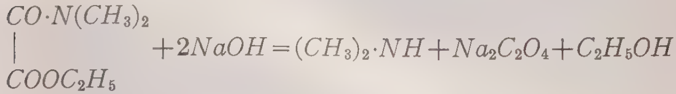
ethyl oxalate

dimethyl oxamic ester

The tertiary compound, trimethyl amine, does not react with ethyl oxalate. The mixture is now heated to a temperature sufficiently high to cause the trimethyl amine to distil but not as high as the boiling points of dimethyl oxamide and dimethyl oxamic ester. The solid oxamide is now separated from the liquid ester by filtration. Each of these compounds is then treated with sodium-hydroxide solution which decomposes them and liberates the amines; thus,



$$\begin{array}{l} CO{\cdot}NH{\cdot}CH_3 \\ | \\ CO{\cdot}NH{\cdot}CH_3 \end{array} + 2NaOH = 2CH_3{\cdot}NH_2 + Na_2C_2O_4$$



$$\begin{array}{l} CO{\cdot}N(CH_3)_2 \\ | \\ COOC_2H_5 \end{array} + 2NaOH = (CH_3)_2{\cdot}NH + Na_2C_2O_4 + C_2H_5OH$$

On distilling the reaction mixture obtained in each case, the amine is recovered. Numerous other methods may be employed for the formation of the amines, but since the compounds involved in the various reactions have not yet been studied, discussion of these methods will be reserved until later.

5. Methyl Amine, $CH_3{\cdot}NH_2$.—Methyl amine occurs naturally in bone oil and in herring brine. It is also obtained by the dry distillation of the molasses residues obtained in the manufacture of beet sugar. One method for the synthesis of methyl amine has been given.

Methyl amine is an inflammable, colorless gas having an ammoniacal odor. Its property of inflammability distinguishes it from ammonia.

It is easily condensed to a liquid boiling at −6° C. Like ammonia, it is very readily soluble in water, 1150 volumes of the gas being soluble in 1 volume of water at 12° C. This solution of methyl amine closely resembles a solution of ammonia in its properties. It is strongly alkaline, and, while it precipitates the metallic hydroxides it does not dissolve the precipitated hydroxides of nickel, cobalt, and cadmium; it does, however, dissolve aluminum hydroxide.

Methyl amine forms salts with acids by direct addition.

6. Dimethyl Amine, $(CH_3)_2NH$ **and Trimethyl Amine,** $(CH_3)_3N$.—A method for the preparation of these amines has been given. Dimethyl amine occurs naturally in herring brine and is also formed by the putrefaction of fish. At ordinary temperatures it is a gas, but it is easily condensed to a liquid that boils at 7° C. and is soluble in water.

Trimethyl amine is found in nature in the blossoms of the hawthorn, the pear, and the wild cherry. It is prepared on a large scale from herring brine. Trimethyl amine is a colorless liquid that boils at 3.5° C. and has a strong fishy odor. It is readily soluble in water and alcohol, is inflammable, and, like ammonia, forms salts with acids.

7. Ethyl Amines.—The ethyl amines resemble the methyl amines very closely. They can be made by the action of ammonia on ethyl iodide, and are separated from each other precisely as are the methyl amines.

Ethyl amine, $(C_2H_5)NH_2$, is a colorless inflammable liquid, with a pungent ammoniacal odor and a burning taste. It boils at 19° C. and has a specific gravity of .7057 at 0° C. It mixes with water in all proportions and has the property of expelling ammonia from ammonium salts. The aqueous solution of ethyl amine is caustic and, when in excess, dissolves aluminum and copper hydroxides.

Diethyl amine, $(C_2H_5)_2NH$, is a volatile, colorless, inflammable, and strongly alkaline liquid. It is soluble in water and alcohol, boils at 56° C., and has a specific gravity of .7226 at 4° C.

Triethyl amine, $(C_2H_5)_3N$, is a colorless, strongly alkaline liquid, with a rather pleasant odor. It is only slightly soluble in water, boils at 90° C., and has a specific gravity of .725 at 25° C. It resembles ammonia in many of its reactions with the salts. However, it is distinguished from ammonia by the fact that it dissolves aluminum hydroxide but does not dissolve silver oxide, which is quite readily soluble in ammonia.

8. Tetramethyl Ammonium Hydroxide, $(CH_3)_4N\cdot OH$. Tetramethyl ammonium hydroxide is prepared by the addition of methyl iodide to the tertiary methyl amine, when the tetramethyl ammonium iodide is formed. When treated with moist silver oxide, tetramethyl ammonium iodide yields tetramethyl ammonium hydroxide. This reaction is shown by the equation,

$$2(CH_3)_4NI + Ag_2O + H_2O = 2(CH_3)_4N\cdot OH + 2AgI$$

The hydroxide is obtained in the form of deliquescent needles that are soluble in water and alcohol and have a strong alkaline reaction. It readily absorbs carbon dioxide and is decomposed by heat into trimethyl amine and methyl alcohol; thus,

$$(CH_3)_4N\cdot OH = (CH_3)_3N + CH_3OH$$

9. Distinction Between Amines.—Primary, secondary, and tertiary amines may be distinguished from one another by their behavior when acted on by nitrous acid. The methyl amines will be taken for purposes of illustration. When nitrous acid acts on a primary amine, an alcohol and water are formed and nitrogen is liberated. Thus,

$$CH_3NH_2 + HNO_2 = CH_3OH + H_2O + N_2$$

With a secondary amine, a *nitroso* compound is formed,

$$(CH_3)_2NH + HNO_2 = \underset{\text{dimethyl-nitrosoamine}}{(CH_3)_2N\cdot NO} + H_2O$$

Dimethyl nitrosoamine is a yellow liquid of an oily nature, boiling at about 151° C.

Tertiary amines are not acted on by nitrous acid.

10. Hydrazines.—The hydrazines bear the same relation to hydrazine, N_2H_4, or diamide, $H_2N—NH_2$, as the substituted ammonias do to ammonia. The hydrazines had been investigated by Emil Fischer long before hydrazine was obtained in the free state. Up to the present time it has only been possible to replace two hydrogen atoms by an alkyl radical, but the other two may be replaced by aromatic residues. These are the best-known hydrazines, and they will be more fully discussed when the study of the compounds of the benzene or aromatic series is taken up.

The hydrazines are similar to the amines in that they are liquids, have the odor of ammonia, possess strong basic properties, and are capable of reducing ammoniacal solutions of copper oxide. They are divided into two classes: primary hydrazines, $N\cdot HR—NH_2$, and secondary hydrazines, $N\cdot R_2—NH_2$.

NITRO COMPOUNDS

11. Preparation and Structure.—The nitro compounds contain the radical, NO_2, and are isomeric with the ethereal salts or esters of nitrous acid. Nitro compounds of the aliphatic series, cannot be prepared by the direct treatment of the hydrocarbon with nitric acid, but are obtained when silver nitrite acts on an alkyl halide. Thus,

$$RI+AgNO_2=R\cdot NO_2+AgI$$

When this reaction takes place two compounds with the same empirical formula, but different boiling points, are formed. The compound of lower boiling point is an ester, since it is decomposed into an alcohol and nitrous acid by the action of caustic potash, and under the influence of reducing agents is converted into an alcohol and ammonia. The compound having the higher boiling point is not, however, converted into an alcohol and nitrous acid by the action of caustic potash, but upon reduction it forms a primary amine. This reaction is shown by the equation

$$R\cdot NO_2+3H_2=R\cdot NH_2+2H_2O$$

The hydrogen atoms of an amine are directly connected to nitrogen, and, since in the foregoing reaction, the two oxygen atoms in the nitro compound have been replaced by two hydrogen atoms to form an amine, it is evident that the oxygen atoms in the nitro compound are also directly connected to nitrogen. Again, the reduction to an amine takes place at ordinary temperatures, and when oxygen is connected to carbon, as in an alcohol or an ether, it cannot be replaced at low temperatures. Therefore, it is evident that nitro compounds contain the group NO_2, in which nitrogen is directly linked to carbon. The structural formula for a nitro compound may then be written, $R\cdot NO_2$, and that for the alkyl nitrite is $R\cdot O\cdot NO$, in which nitrogen is directly linked to oxygen.

12. General Properties.—The nitroparaffins are colorless liquids with an ethereal odor, the lower members are slightly soluble in water, but all distil without decomposition. They also have one hydrogen atom replaceable by sodium, which compound is insoluble in absolute alcohol. This insolubility is frequently taken advantage of to separate the nitroparaffins from other substances.

13. Nitromethane, CH_3NO_2.—Nitromethane is prepared by treating methyl iodide with silver nitrite; thus,

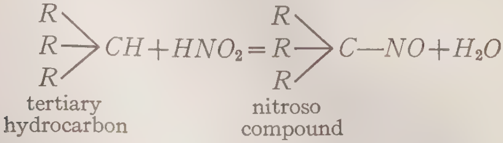
$$CH_3I + AgNO_2 = CH_3 \cdot NO_2 + AgI$$

It is obtained in the form of a heavy colorless liquid with a peculiar odor. It is soluble in alcohol and ether, boils at 101° C., and has a specific gravity of 1.144 at 15° C.

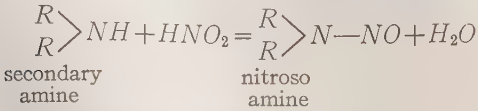
14. Nitroethane, $C_2H_5NO_2$.—Nitroethane is prepared in the same manner as nitromethane. It is obtained, together with some ethyl nitrite, in the form of an oily liquid that has a pleasant ethereal odor. These products are separated by fractional distillation, the ethyl nitrite boiling at 17° C., while the nitroethane boils at 114° C. Its specific gravity, at 15° C., is 1.056.

NITROSO COMPOUNDS

15. The nitroso compounds contain the NO group. They are formed whenever a tertiary hydrocarbon or a secondary amine is acted on by nitrous acid. Thus,



$$\underset{\text{tertiary hydrocarbon}}{\left.\begin{matrix}R\\R\\R\end{matrix}\right> CH} + HNO_2 = \underset{\text{nitroso compound}}{\left.\begin{matrix}R\\R\\R\end{matrix}\right> C{-}NO} + H_2O$$



$$\underset{\text{secondary amine}}{\left.\begin{matrix}R\\R\end{matrix}\right> NH} + HNO_2 = \underset{\text{nitroso amine}}{\left.\begin{matrix}R\\R\end{matrix}\right> N{-}NO} + H_2O$$

On reduction, nitroso compounds, like the nitro compounds, are converted into amines.

CYANOGEN AND ITS COMPOUNDS

16. Acids and Salts of Cyanogen.—While neither cyanogen, $(CN)_2$, nor its acids and salts can be considered as derivatives of the hydrocarbons, yet they form the starting point for the synthesis of so many important organic compounds which are derivatives of hydrocarbons, that they will be considered at this point.

17. Potassium Ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$.—Potassium ferrocyanide is obtained when organic substances containing nitrogen, such as refuse animal matter, are heated with iron filings and potassium carbonate. The product thus obtained is leached or extracted with water, the potassium ferrocyanide being recovered by crystallization from this solution. The crystals are large and of a yellow color. They have a salty taste and effloresce upon exposure to air. The water of crystallization can be driven off between 60° C., and 80° C., leaving a white powder. Potassium ferrocyanide is not poisonous. It is an important compound because it may be used as a starting point for the preparation of all compounds containing cyanogen.

18. Potassium Ferricyanide, $K_3Fe(CN)_6$.—Potassium ferricyanide is made by passing chlorine through a solution of potassium ferrocyanide. The anhydrous crystals obtained from this solution are bright red in color and are poisonous. Potassium ferricyanide is an excellent oxidizing agent in alkaline solutions. Reducing agents convert it to potassium ferrocyanide. Potassium ferricyanide is also known as *red prussiate of potash*.

19. Potassium Cyanide, KCN.—Potassium cyanide is obtained when anhydrous potassium ferrocyanide is heated to redness in stoneware retorts.

$$K_4Fe(CN)_6 + \text{heat} = 4KCN + FeC_2 + N_2$$

As only two-thirds of the cyanogen is obtained in the form of potassium cyanide, however, the usual method employed to obtain a larger yield is to fuse a mixture of potassium carbonate and potassium ferrocyanide,

$$K_4Fe(CN)_6+K_2CO_3=5KCN+KOCN+CO_2+Fe$$

Potassium cyanide is also made by heating potassium carbonate and carbon in an atmosphere of ammonia,

$$K_2CO_3+C+2NH_3=2KCN+3H_2O$$

The fused mass is treated with alcohol which dissolves out the potassium cyanide, after which the alcohol is evaporated and the potassium cyanide recovered.

Potassium cyanide is an extremely poisonous, white, amorphous, deliquescent solid having an odor of hydrocyanic acid and a caustic taste. When it is boiled with water, hydrocyanic acid and caustic potash are formed,

$$KCN+H_2O=HCN+KOH$$

20. Hydrocyanic Acid, HCN.—Hydrocyanic, or prussic, acid was discovered by Gay-Lussac in 1811. It occurs naturally, but only in traces, in bitter almonds and in the kernels of many fruit stones, such as the peach and cherry. Hydrocyanic acid is one of the most deadly poisons known. If the volatile free acid is inhaled, death is the usual result.

An aqueous solution of hydrocyanic acid is prepared by distilling a concentrated solution of potassium cyanide with dilute sulphuric acid, and absorbing the vapors in water.

Hydrocyanic acid, when pure, is a colorless, stable liquid with an odor of bitter almonds. It boils at 26° C., solidifies at −14° C., and is very volatile. It is soluble in water, alcohol, and ether. The aqueous solution of hydrocyanic acid is very unstable, decomposing, on standing, with the formation of *ammonium formate*.

21. Mercuric Cyanide, $Hg(CN)_2$.—Mercuric cyanide is prepared by the action of an aqueous solution of hydrocyanic acid on mercuric oxide,

$$HgO+2HCN=Hg(CN)_2+H_2O$$

It crystallizes from solution in the form of colorless, transparent prisms which have a bitter metallic taste. Mercuric cyanide is very poisonous. On being heated, it decomposes, with the formation of mercury and cyanogen.

22. Cyanogen, $(CN)_2$.—When an organic compound containing nitrogen is heated with metallic sodium, cyanogen and sodium cyanide are formed,

$$2N_2+4C+2Na=2NaCN+(CN)_2$$

Cyanogen is also obtained when mercuric cyanide is decomposed by heat,

$$Hg(CN)_2=Hg+(CN)_2$$

In this reaction, a brown, amorphous polymeride, *paracyanogen*, $(CN)_x$, is first formed, which, on further heating is converted into cyanogen. This reaction is similar to the decomposition of mercuric oxide in preparing oxygen.

Probably the better method for the preparation of cyanogen is by the treatment of copper sulphate with potassium cyanide; thus,

$$2CuSO_4+4KCN=Cu_2(CN)_2+2K_2SO_4+(CN)_2$$

It is also obtained when ammonium oxalate is subjected to dry distillation,

$$(NH_4)_2C_2O_4=4H_2O+(CN)_2$$

Cyanogen is named from the Greek word *kyanos*, blue, because several of its compounds have that color. It is a colorless gas with a characteristic odor resembling bitter almonds. It is easily condensed to a colorless liquid that boils at −20.7° C. It is extremely poisonous and inflammable, burning with a pale, purplish flame. Cyanogen is soluble in one-fourth its volume of water, but this solution is unstable, decomposing into ammonia, urea, hydrocyanic acid, carbon dioxide, and oxalic acid.

In some of its reactions, cyanogen is very similar to the halogens, as its preparation from copper sulphate and potassium cyanide shows. When chlorine is passed into caustic potash, the chloride and hypochlorite are formed, and when cyanogen is passed into caustic potash, the cyanide and cyanate are formed; thus,

$$2KOH+(CN)_2=KCN+KCNO+H_2O$$

23. Structure of Cyanogen.—That cyanogen has the structure indicated by the formula $N{\equiv}C{-}C{\equiv}N$, in which carbon is tetravalent and nitrogen trivalent, is shown by the fact that when hydrolyzed, it takes up 4 molecules of water and yields oxalic acid and ammonia which, in turn, react to form ammonium oxalate. Thus,

$$(CN)_2+4H_2O=(NH_4)_2C_2O_4$$

and when ammonium oxalate is treated with a dehydrating agent the reverse action takes place and cyanogen is formed.

HALOGEN COMPOUNDS OF CYANOGEN

24. Cyanogen Chlorides, $CNCl$ and $C_3N_3Cl_3$.—Two chlorides of cyanogen are known, one a liquid and the other a solid. The liquid cyanogen chloride is made by passing chlorine over mercuric cyanide. It is also obtained by passing chlorine into a dilute solution of hydrocyanic acid at 0° C.; thus,

$$HCN+Cl_2=CNCl+HCl$$

When the solution has become saturated with chlorine, it is distilled over calcium chloride and collected in a well-cooled receiver. It is a colorless volatile liquid that boils at 15.5° C., has a penetrating odor, and is very irritating to the eyes. It polymerizes readily into the solid cyanogen chloride, or cyanuric chloride.

Liquid cyanogen chloride under the action of caustic potash is converted into potassium cyanate and potassium chloride; thus,

$$CNCl+2KOH=KCNO+KCl+H_2O$$

Solid cyanogen chloride, $C_3N_3Cl_3$, is also obtained by treating anhydrous hydrocyanic acid with chlorine in direct sunlight; the chloride then crystallizes in bright yellow needles or plates. It melts at 140° C., and boils at 190° C. It has a peculiar irritating odor and is decomposed by boiling water into cyanuric acid and hydrochloric acid; thus,

$$C_3N_3Cl_3+3H_2O=(HNCO)_3+3HCl$$

Cyanogen bromide and cyanogen iodide are also known, being made by the action of bromine and iodine on mercuric cyanide.

CYANOGEN ACIDS AND SALTS

25. Cyanuric Acid, $(HNCO)_3$.—Cyanuric acid is made by heating urea,

$$3CO(NH_2)_2 = 3NH_3 + (HNCO)_3$$

A better yield is obtained, however, by passing dry chlorine over urea kept in fusion by a gentle heat; thus,

$$6CO(NH_2)_2 + 3Cl_2 = 4NH_4Cl + 2HCl + N_2 + 2(HNCO)_3$$

Cyanuric acid is a white crystalline solid that is soluble in water and alcohol. It crystallizes from its boiling solutions in prisms containing two molecules of water. It is a tribasic acid and is decomposed by heat.

26. Isocyanic Acid, $HNCO$.—Isocyanic acid is prepared by heating its polymeride, cyanuric acid, and cooling the resulting vapors by means of a freezing mixture. This acid is ordinarily known as *cyanic acid*. Below 0° C., isocyanic acid is a colorless liquid that has a strong, irritating odor, resembling that of acetic acid. Above 0° C. it is very unstable and is converted into a white amorphous solid, the change being accompanied with violent ebullition and a crackling noise. This solid is known as *cyamelide* and is a polymeride of isocyanic acid with the probable formula $(HNCO)_3$.

The aqueous solution of isocyanic acid decomposes readily into ammonia and carbon dioxide; thus,

$$HNCO + H_2O = NH_3 + CO_2$$

The salts of isocyanic acid are soluble in water, but, like the acid, they are unstable, breaking down into ammonia and the acid carbonate.

When a solution of ammonium cyanate, NH_4OCN, is evaporated to dryness, a rearrangement of the molecule takes place, and urea, $CO(NH_2)_2$ is formed. This reaction is of historical interest, since urea was the first organic compound to be prepared synthetically.

27. Isomerism of Cyanic Acids.—Cyanic acid is known only by its salts. These have the structure illustrated by the formula for potassium cyanate, $K-O-C\equiv N$. The acid should accordingly have the structure, $H—O—C\equiv N$. Another acid is known, however, that has the same composition as cyanic acid but a different structure. The isomeride is isocyanic acid and has the structure indicated by the formula $H—N=C=O$. When this acid is neutralized with potassium hydroxide, however, a salt having the structure of potassium isocyanate, $K—N=C=O$, is *not* obtained, but the normal cyanate, $K—O—C\equiv N$, is formed. Thus, while cyanic acid is unknown, its salts are known, and although isocyanic acid actually exists, the salts formed from it are normal cyanates. In other words, salts, such as potassium isocyanate, $K—N=C=O$, are unknown.

28. Thiocyanic Acid, $HSCN$.—Thiocyanic acid closely resembles cyanic acid in its properties, but it is more stable. It is prepared by decomposing barium thiocyanate with sulphuric acid. The solution is fractionated, the vapor passed over calcium chloride and collected in a receiver surrounded by a freezing mixture. The anhydrous acid is a volatile, colorless liquid with a well-defined odor of horseradish. When removed from the freezing mixture, it quickly changes into a solid polymeride.

ALKYL CYANIDES OR NITRILES

29. Structure.—When alkyl halides such as methyl iodide and ethyl iodide are treated with potassium cyanide, compounds which are cyanides of the hydrocarbons and have the compositions C_2H_3N and C_3H_5N are formed. When these compounds are boiled with water (hydrolyzed), ammonia and acetic and propionic acids are formed. Thus,

$$C_2H_3N+2H_2O=NH_3+CH_3COOH$$
$$C_3H_5N+2H_2O=NH_3+C_2H_5COOH$$

In these acids each carbon atom is linked to the other, and it follows, that in the compounds C_2H_3N and C_3H_5N the carbon atoms must likewise be connected to each other. Therefore, the only possible formulas for these compounds are: *methyl cyanide*, $CH_3{\cdot}CN$, and *ethyl cyanide*, $C_2H_5{\cdot}CN$, in which the carbon atoms are linked together and nitrogen is linked to one carbon. The general formula for the alkyl cyanides or nitriles is, then, $R—C\equiv N$.

30. Methyl Cyanide, CH_3CN.—Methyl cyanide or acetonitrile, is prepared by distilling a mixture of potassium methyl sulphate with potassium cyanide. The reaction is shown by the equation

$$CH_3 \cdot KSO_4 + KCN = CH_3CN + K_2SO_4$$

Another method of preparing this substance is to heat a mixture of methyl iodide and potassium cyanide; in this case, the reaction is

$$CH_3I + KCN = CH_3CN + KI$$

Methyl cyanide is made on a large scale by the treatment of acetamide with either acetic anhydride or glacial acetic acid. The acetic anhydride removes one molecule of water from the acetamide, according to the reaction

$$\underset{\text{acetamide}}{CH_3 \cdot CONH_2} + (CH_3 \cdot CO)_2O = CH_3CN + 2CH_3COOH$$

Methyl cyanide is a colorless, volatile liquid that has a pleasing aromatic odor and a specific gravity of .789 at 15° C. It is soluble in alcohol and water and boils at 82° C. A boiling solution of caustic potash decomposes methyl cyanide according to the equation

$$CH_3CN + KOH + H_2O = CH_3 \cdot COOK + NH_3$$

31. Ethyl Cyanide, C_2H_5CN.—Ethyl cyanide, or propionitrile, is formed when ethyl potassium sulphate is distilled with potassium cyanide. The reaction is shown by the equation

$$C_2H_5 \cdot KSO_4 + KCN = C_2H_5CN + K_2SO_4$$

It is also prepared by heating ethyl chloride with potassium cyanide.

Ethyl cyanide is a colorless liquid and has a characteristic ethereal odor. Its specific gravity at 0° C. is .801, and its boiling point 97° C. It is soluble in water and alcohol and is poisonous. When treated with caustic potash, ethyl cyanide forms potassium propionate and ammonia; thus,

$$C_2H_5CN + KOH + H_2O = C_2H_5 \cdot COOK + NH_3$$

This property of the cyanides is of great value in organic chemistry, as it makes possible the formation of an acid from an alcohol containing one carbon atom less than does the acid. When treated with nascent hydrogen, the alkyl cyanides are converted into primary amines. Thus,

$$CH_3CN + 4H = CH_3 \cdot CH_2 \cdot NH_2$$

ALKYL ISOCYANIDES OR CARBYLAMINES

32. Isomerism and Structure.—As previously stated, the alkyl cyanides are formed when an alkyl halide is treated with potassium cyanide. Thus,

$$CH_3I + KCN = CH_3CN + KI$$

When the reaction takes place between the alkyl halide and silver cyanide, however, a compound having the same empirical formula as methyl cyanide, C_2H_3N, but having different properties, is formed. This isomeride is called *methyl isocyanide*.

The manner in which carbon and nitrogen are linked together in alkyl cyanides has been discussed. It was also shown that when methyl cyanide is hydrolyzed, ammonia and acetic acid are formed. Thus,

$$CH_3CN + 2H_2O = NH_3 + CH_3COOH$$

Obviously the linkage between the carbon atoms in methyl cyanide and in acetic acid remains unchanged as the result of the reaction. Nitrogen, however, leaves the carbon atom to which it is attached and unites with hydrogen to form ammonia.

When the isomeride obtained as the result of the reaction between methyl iodide and silver cyanide is treated with water, methyl amine and formic acid are the products of the reaction. Thus,

$$C_2H_3N + 2H_2O = CH_3NH_2 + HCOOH$$

Here it is seen that the nitrogen atom does not leave the carbon atom to which it is attached; instead, the linking between the two carbon atoms has been broken.

33. From the formation of the alkyl amines by the action of alcoholic ammonia on alkyl iodides, it is known that the nitrogen atom of the amino group is directly connected to the carbon atom of the alkyl radical. Therefore, since methyl amine is also formed when the compound obtained by the action of silver cyanide on methyl iodide, is hydrolyzed, it follows that the nitrogen atom in methyl isocyanide is also connected to the carbon atom of the methyl radical. The formula for methyl isocyanide would accordingly be CH_3NC and the general formula for the alkyl isocyanides would be $R—N{\equiv}C$.

34. Preparation.—The isocyanides can be prepared in a pure condition by the action of chloroform and caustic potash upon the primary amines, as is shown by the equation

$$RNH_2+CHCl_3+3KOH=R{\cdot}NC+3KCl+3H_2O$$

This reaction affords a very delicate test for the primary amines due to the disagreeable and characteristic odor of the isocyanides. Secondary and tertiary amines are not converted into isocyanides by this reaction.

35. Methyl and Ethyl Isocyanides, CH_3NC and C_2H_5NC. Methyl and ethyl isocyanides are prepared by treating the iodine substitution product with silver cyanide, or by the action of chloroform and caustic potash on methyl or ethyl amine. Their chemical properties are identical. When treated with dilute acids, they are decomposed into formic acid and the corresponding amine, the action being one of simple hydrolysis, the acid not taking part in the reaction:

$$CH_3NC+2H_2O=CH_3NH_2+H{\cdot}COOH$$
$$C_2H_5NC+2H_2O=C_2H_5NH_2+H{\cdot}COOH$$

These isocyanides are all colorless liquids and with difficulty are decomposed by the caustic alkalies. Methyl isocyanide boils at 60° C., and ethyl isocyanide boils at 82° C.

CYANATES AND ISOCYANATES

36. Isomerism and Structure.—The cyanates and isocyanates bear the same relation to cyanic acid that the cyanides and isocyanides bear to hydrocyanic acid. The same views are held in regard to their structure as are held in regard to that of the cyanides and isocyanides. The cyanates are obtained by passing cyanogen chloride into an alcoholate; thus,

$$R{\cdot}O{\cdot}K+CNCl=R{\cdot}O{\cdot}CN+KCl$$

This equation shows that the radical is united to the cyanogen by the oxygen. This union is also shown by the fact that the cyanates decompose into a cyanate and alcohol when acted on by caustic alkalies or dilute acids; thus,

$$R{\cdot}O{\cdot}CN+KOH=K{\cdot}O{\cdot}CN+R{\cdot}OH$$

On the other hand, the isocyanates, which are prepared by distilling an alkyl potassium sulphate with potassium cyanate, are believed to have the constitutional formula $R{\cdot}N{:}CO$, the radical being united to the carbon by means of the nitrogen. They are made, in the same manner as the isocyanides, by treating the alkyl iodides with silver cyanate. This view of the constitution of the isocyanates is upheld by the products of their decomposition, namely, an amine and carbon dioxide, as is shown by the equation

$$R—N{=}CO+H_2O=R{\cdot}NH_2+CO_2$$

37. Potassium Cyanate, $KOCN$.—Potassium cyanate is obtained in the form of small white needles by passing cyanogen chloride into a well-cooled solution of caustic potash. Potassium cyanate is also formed by heating to dull redness a mixture of manganese dioxide and potassium ferrocyanide.

$$K_4Fe(CN)_6+\text{heat}=4KCN+FeC_2+N_2$$
$$KCN+O=KOCN$$

After fusion, the mixture is cooled and dissolved in boiling alcohol. On cooling, the potassium cyanate deposits in laminated transparent crystals, which are very soluble in water. Hydrochloric acid decomposes the aqueous solution, evolving carbon dioxide and cyanic acid.

38. Methyl and Ethyl Cyanates.—Methyl and ethyl cyanate, $CH_3.O.CN$, and $C_2H_5.O.CN$, have not been isolated. They are prepared, however, by treating the sodium or potassium alcoholate with cyanogen chloride.

39. Methyl and Ethyl Isocyanates.—Methyl and ethyl isocyanate, $CH_3{\cdot}N{:}CO$ and, $C_2H_5{\cdot}N{:}CO$, are well known, and are prepared by the action of silver cyanate on their iodine substitution products. They are volatile liquids, with a disagreeable penetrating odor, and boil without decomposition. On standing they polymerize, yielding isocyanurates. Methyl isocyanate boils at 44° C. and ethyl isocyanate boils at 60° C. Treated with dilute alkalies or dilute acids, they decompose into the amine and carbon dioxide.

$$CH_3{\cdot}N{:}CO+H_2O=CO_2+CH_3{\cdot}NH_2$$
$$C_2H_5{\cdot}N{:}CO+H_2O=CO_2+C_2H_5{\cdot}NH_2$$

40. Fulminic Acid, $HONC$.—Fulminic acid is obtained when its salts are treated with strong acids, but it combines readily with the latter, taking up water and forming hydroxyl amine and formic acid. Fulminic acid is a very unstable, volatile, poisonous substance, which has an odor strongly resembling that of hydrocyanic acid. Fulminic acid is isomeric with cyanic acid.

41. Mercury Fulminate, $Hg(ONC)_2$.—Mercury fulminate is prepared by dissolving mercury in nitric acid and adding alcohol to the hot solution. In a few minutes, a brisk effervescence takes place, and the fulminate of mercury is deposited in the form of a white powder that is safe to handle while wet, but, when dry, is very explosive. Mercury fulminate is used as a detonator in percussion caps.

THIOCYANATES

42. Potassium Thiocyanate, $KSCN$.—Potassium thiocyanate is obtained, in the form of long prismatic crystals, by boiling a solution of potassium cyanide with sulphur. It is deliquescent and very soluble in water and alcohol. When heated with dilute sulphuric acid, potassium thiocyanate decomposes similarly to cyanic acid, yielding carbon oxysulphide instead of carbon dioxide; thus,

$$KSCN+2H_2SO_4+H_2O=KHSO_4+NH_4HSO_4+COS$$

43. Ethereal Salts of Thiocyanic Acid.—The ethereal salts, or esters, of thiocyanic acid are usually made by one of the three following methods:

1. By distilling the corresponding alkyl potassium sulphate with potassium thiocyanate; thus,

$$R\cdot KSO_4+KSCN=R\cdot SCN+K_2SO_4$$

2. By heating potassium thiocyanate with the alkyl halides; thus,

$$KSCN+R\cdot I=R\cdot SCN+KI$$

3. By the action of cyanogen chloride upon salts of the mercaptans; thus,

$$R\cdot SK+CNCl=R\cdot SCN+KCl$$

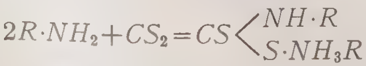
These salts are liquids and are insoluble in water. Oxidizing agents such as nitric acid, convert them into the corresponding alkyl sulphonic acid. When treated with nascent hydrogen, they are reduced to mercaptans, as is shown by the equation

$$R\cdot SCN+2H=R\cdot SH+HCN$$

These two reactions prove that the sulphur is in direct combination with the hydrocarbon radical; hence, the constitution of the thiocyanates must be represented by the formula $R—S—CN$. Heating the thiocyanates converts them into the isomeric isothiocyanates, or mustard oils.

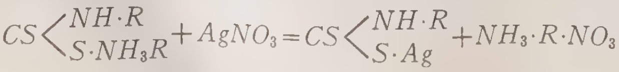
ISOTHIOCYANATES

44. The **isothiocyanates,** isomeric with the thiocyanates, are also called *mustard oils*, from their most important representative, allyl isothiocyanate. They are prepared by heating the thiocyanates causing a rearrangement of the molecule and by the action of a primary amine upon carbon disulphide in an alcoholic or ethereal solution, as is shown by the equation



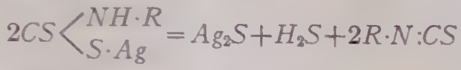
$$2R\cdot NH_2+CS_2=CS\left\langle\begin{matrix}NH\cdot R\\S\cdot NH_3R\end{matrix}\right.$$

forming the alkyl ammonium salt of alkyl thiocarbamic acid. This substance is then treated with silver nitrate, forming the silver salt; thus,



$$CS\left\langle\begin{matrix}NH\cdot R\\S\cdot NH_3R\end{matrix}\right.+AgNO_3=CS\left\langle\begin{matrix}NH\cdot R\\S\cdot Ag\end{matrix}\right.+NH_3\cdot R\cdot NO_3$$

This compound, upon distillation, breaks up yielding silver sulphide, hydrogen sulphide, and mustard oil. This reaction is shown by the equation



$$2CS\left\langle\begin{matrix}NH\cdot R\\ S\cdot Ag\end{matrix}\right.=Ag_2S+H_2S+2R\cdot N:CS$$

The isothiocyanates have the alkyl radical attached to the nitrogen, and hence have the constitutional formula $R—N=CS$. This is borne out by the following facts:

1. When an isothiocyanate, or mustard oil, is treated with nascent hydrogen (reduced), it is converted into a primary amine and thioformaldehyde; for example,

$$R\cdot N:CS+4H=R\cdot NH_2+CH_2S$$

2. When an isothiocyanate, or mustard oil, is treated with dilute sulphuric acid, it takes up water, yielding a primary amine and carbon oxysulphide; for example,

$$R\cdot N:CS+H_2O=R\cdot NH_2+COS$$

ALKYL COMPOUNDS OF METALS AND NON-METALS

ORGANO-METALLIC COMPOUNDS

45. Introductory.—Some of the metals and non-metals that form the more important compounds with alkyl groups are magnesium, zinc, lead, arsenic, and phosphorus. The compounds that they form are used to a large extent in organic synthesis.

46. Ethyl Magnesium Iodide, C_2H_5MgI.—Ethyl magnesium iodide was first used for the purpose of synthesis by Grignard in 1900. It is accordingly called the *Grignard reagent*. It is prepared by bringing magnesium turnings in contact with a dry ethereal solution of an alkyl iodide. When ethyl iodide is used, the reaction may be represented as follows:

$$2C_2H_5I+2Mg=2C_2H_5MgI$$

When treated with water, ethyl magnesium iodide decomposes with the formation of ethane, magnesium iodide, and magnesium hydroxide.

$$2C_2H_5MgI+2H_2O=2C_2H_6+MgI_2+Mg(OH)_2$$

Reactions in which the Grignard reagent is used will be described from time to time.

47. Zinc Ethyl, $Zn(C_2H_5)_2$.—Compounds of methane and ethane with zinc were discovered by Frankland in 1849. They react readily, and form an important class of organo-metallic compounds. They are colorless liquids with disagreeable odors, fume strongly in the air, and ignite readily. They cause painful wounds when brought in contact with the skin and must be handled in an atmosphere of carbon dioxide.

Zinc ethyl is prepared by the action of zinc on ethyl iodide. The reaction takes place in two stages; the first stage is shown by the equation

$$Zn+C_2H_5I=Zn(C_2H_5)I$$

This product is then distilled when zinc ethyl and zinc iodide are formed, as is shown by the equation

$$2Zn(C_2H_5)I=Zn(C_2H_5)_2+ZnI_2$$

Zinc ethyl is a colorless liquid, with a peculiar penetrating odor. It boils at 118° C., has a specific gravity of 1.18 at 15° C., takes fire on contact with the air, burning with a greenish flame and evolving white fumes, and is decomposed violently by water.

Reactions in which a zinc alkyl compound takes part are known as *Frankland reactions*. The following reaction, showing the formation of propane from zinc ethyl and methyl iodide, is typical:

$$Zn(C_2H_5)_2+2CH_3I=ZnI_2+2C_3H_8$$

48. Lead Compounds.—Compounds of lead containing two alkyl groups to one atom of lead are not known. The lead derivatives are produced by the action of zinc ethyl upon lead chloride, and by the action of the alkyl iodides upon an alloy of lead and sodium. Lead tetramethyl, $Pb(CH_3)_4$, is a liquid with a faint odor, is insoluble in water, has a specific gravity of 2.03, and boils at 110° C. When heated with hydrochloric acid, a crystalline compound of lead trimethyl chloride, $Pb(CH_3)_3Cl$, is obtained.

ORGANO-NONMETALLIC COMPOUNDS

49. Arsines.—The compounds of arsenic that are of greatest importance are those in which the three hydrogen atoms of arsine, AsH_3, have been replaced by alkyl radicals. These compounds are known as tertiary arsines and are obtained when arsenious chloride, $AsCl_3$, is treated with a zinc alkyl compound, or when an alkyl iodide is heated with sodium arsenide, $AsNa_3$. The equations representing the reactions that take place are written as follows:

$$2AsCl_3+3Zn(C_2H_5)_2=2As(C_2H_5)_3+3ZnCl_2$$
$$AsNa_3+3CH_3I=As(CH_3)_3+3NaI$$

50. Cacodyl, $As_2(CH_3)_4$.—The best known and most characteristic compound of carbon containing arsenic is that known as *cacodyl*. This name has been given to it from the Greek word for *stinking*, because of its extremely disagreeable odor. *Cacodyl* is also known as *tetramethyl diarsene* and as *dicacodyl*. It is prepared by distilling a mixture of potassium acetate, and arsenious oxide. The reaction is complicated. Cacodyl oxide is first formed; thus,

$$As_2O_3+4CH_3COOK=As_2(CH_3)_4O+2K_2CO_3+2CO_2$$

When cacodyl oxide is treated with hydrochloric acid, cacodyl chloride is formed,

$$As_2(CH_3)_4O+2HCl=2As(CH_3)_2Cl+H_2O$$

Upon treating cacodyl chloride with zinc in an atmosphere of carbon dioxide, cacodyl is produced,

$$2As(CH_3)_2Cl+Zn=As_2(CH_3)_4+ZnCl_2$$

Cacodyl is a heavy, oily, colorless, liquid that crystallizes at −6° C. in large transparent crystals, and boils at 170° C. It is extremely inflammable in the air, and when its vapor is passed through a tube heated to 400° C. it decomposes. Cacodyl oxide, $As_2(CH_3)_4O$, is the original fuming liquor of Cadet, and was discovered by him in 1760. It is an oily liquid with an offensive odor. It has a specific gravity of 1.46 and boils at 150° C. It produces dense white fumes in the air, is very poisonous, and has a strong tendency to take fire spontaneously in the air. Cacodyl oxide is soluble in alcohol and combines with acids to form salts.

51. Phosphines.—Like arsenic, phosphorus also forms primary, secondary, and tertiary phosphines. When ethyl or methyl iodide reacts with phosphonium iodide, PH_4I, in the presence of metallic oxides, preferably zinc oxide, at 150° C., monoethyl phosphine, $PH_2(C_2H_5)$, and diethyl phosphine, $PH(C_2H_5)_2$, are formed. The hydriodides of these compounds are first formed, then water is added to the mixture when the monoethyl phosphine is liberated. After this compound has been expelled by heat, caustic potash is added to the residue, liberating the diethyl phosphine. Monoethyl phosphine is a colorless liquid lighter than water, boils at 25° C., is insoluble in water, and has a most disagreeable odor. It takes fire in contact with chlorine or nitric acid. Diethyl phosphine is also a liquid, is lighter than water, and boils at 85° C.

UNSATURATED HYDROCARBONS OF THE ALIPHATIC SERIES

ETHYLENE, OR OLEFINE, SERIES

52. Introductory.—The hydrocarbons that have been described thus far are known as *saturated compounds* because of their inability to unite directly with other elements and compounds. The general formula for the saturated hydrocarbons of the aliphatic series is C_nH_{2n+2}. It was shown that in order to form derivatives of the saturated compounds, it was first necessary to remove hydrogen. This process is known as *substitution* and the products formed are known as *substitution products*. In the case of unsaturated hydrocarbons, however, derivatives are formed by the direct addition of other elements and compounds. These derivatives are called *addition products*.

53. Structure.—In order to show the structure of the unsaturated hydrocarbons, the first member of the series, ethylene, C_2H_4, will be used for illustrative purposes.

When one of the halogens, chlorine for instance, is brought in contact with ethylene, a reaction takes place and a compound having the formula $C_2H_4Cl_2$, is formed. This compound is the same as one of the two formed when two of the hydrogen atoms of ethane are replaced by chlorine. The two reactions may be represented by the equations:

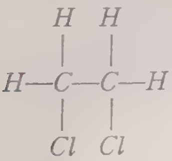
$$C_2H_6+2Cl_2=C_2H_4Cl_2+2HCl$$
$$C_2H_4+Cl_2=C_2H_4Cl_2$$

Thus it is seen that one reaction represents a case of substitution and the other a case of addition.

When the isomerism of the dihalogen ethanes was discussed in a preceding Section, it was shown that two dichlorethanes were possible. One of these was called a *symmetrical compound* because the chlorine atoms were attached to different carbon atoms, the other was called an *unsymmetrical compound* because both of the chlorine atoms were attached to the same carbon atom. The positions occupied by the chlorine atoms in each compound can be shown by different reactions. When they are treated with potassium hydroxide, only one of them reacts to form acetaldehyde, CH_3CHO; thus,

$$C_2H_4Cl_2+KOH=CH_3CHO+KCl+HCl$$

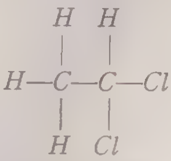
The formulas for the two dichlorethanes are



$$H-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H$$

symmetrical

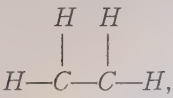
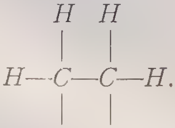
and

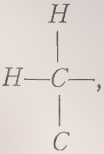


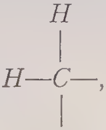
$$H-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-Cl$$

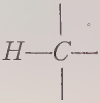
unsymmetrical

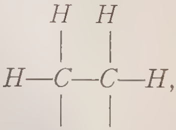
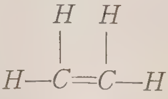
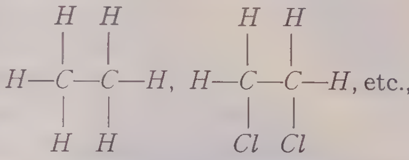
The unsymmetrical compound contains the group CH_3, as does acetaldehyde. Therefore it must be the unsymmetrical compound that reacts with KOH to form CH_3CHO. The dichlorethane obtained by treating ethylene with chlorine has the same properties as does symmetrical dichlorethane. Consequently, the formula for ethylene must be C_2H_4.

54. Double Bond.—It is evident that if the formula C_2H_4, or  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \end{array}$, represents the correct structure of the ethylene molecule, carbon in this compound cannot be tetravalent. It also indicates that ethylene is a saturated compound, which it is not, since it is necessary to add two atoms to it in order to obtain a saturated compound. The above formula does not, then, represent the true structure of ethylene. Considering both the tetravalency of the carbon atom and the unsaturation of this compound, the simplest formula that combines both of these features is,  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \end{array}$. In this formula unsaturation is indicated by the free bonds of valence of the two carbon atoms. However, the theory of free bonds of valence is not borne out by experimental evidence. Thus it has always been impossible to prepare such compounds as


$\begin{array}{cccc} & & H & \\ & & | & \\ H & - & C & - \\ & & | & \\ & & C & \end{array}$,


$\begin{array}{cccc} & & H & \\ & & | & \\ H & - & C & - \\ & & | & \end{array}$, or


$\begin{array}{cccc} & & | & \\ H & - & C & - \\ & & | & \end{array}$

Unsaturated hydrocarbons containing one carbon atom, as far as is known, do not exist. In the case of an unsaturated compound containing two carbon atoms, each of which possesses an unsatisfied valence, as in  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \end{array}$, it is thought probable that the unsatisfied valences will tend to satisfy each other. Each of the unsatisfied bonds must then have some sort of connection with the other and this is shown graphically by representing the structure as  $\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & = & C & - & H \end{array}$, the double bond being used to indicate unsaturation. It should not be thought, however, that a double linking between two atoms indicates the strength of the union. In fact, the contrary is true. A double linking indicates an actual weakness that, according to the theory, is due to the strained condition of the linking. In other words, if the carbon atoms in the saturated compounds  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$, $H-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H$, etc., have certain affinities for hydrogen, chlorine, and other elements, and when these elements are removed, the unsatisfied bonds tend to satisfy each other, it may be assumed that this is an enforced adjustment for the two carbon atoms; if an opportunity is given, they will readily set aside the enforced and unstable linking for a saturated and more permanent one.

55. Occurrence and Preparation of Olefines.—The olefines occur in nature in petroleum, and are formed by the dry distillation of wood, coal, etc. They are also formed by: (1) the elimination of water from the saturated alcohols, by means of dehydrating agents such as sulphuric acid or zinc chloride; (2) the action of an alcoholic solution of caustic potash on a halide of the paraffin series.

56. General Properties.—The olefines are unsaturated hydrocarbons containing a pair of carbon atoms that are doubly linked. They yield derivatives similar to those of the saturated hydrocarbons; though, as compared with the latter and their derivatives, they are few in number, and only a few are of much importance. The members of this series are homologous with ethylene. Their nomenclature differs from that of the corresponding saturated hydrocarbons only by the substitution of the suffix *ylene* for *ane*. They bear a simple relation to the members of the methane series, each member containing two atoms of hydrogen less than the corresponding saturated hydrocarbon and the same number of carbon atoms. Their composition is expressed by the general formula C_nH_{2n}.

Table I gives the name, symbol, and some of the physical properties of some of the members of the olefine series.

The three lowest members of this series are gases, slightly soluble in water; the higher members are all liquids, with the exception of a few of the highest members, which are solids. The higher members, from C_5H_{10} up, are insoluble in water, but soluble in alcohol and ether. Their most important property is their ability to form addition products. The simplest member of this series, methylene, CH_2, has never been obtained. Repeated attempts have been made to prepare it by the removal of HCl from methyl chloride. Such attempts, however, have always resulted in the formation of ethylene, two CH_2 groups uniting to form one molecule of C_2H_4.

TABLE I

MEMBERS OF THE OLEFINE SERIES

Name	Formula	Boiling Point Degrees C.
Ethylene	C_2H_4	−103
Propylene	C_3H_6	− 48
Butylene	C_4H_8	2
Amylene	C_5H_{10}	40
Hexylene	C_6H_{12}	68
Heptylene	C_7H_{14}	98
Octylene	C_8H_{16}	123
Nonylene	C_9H_{18}	139
Decylene	$C_{10}H_{20}$	172
Undecylene	$C_{11}H_{22}$	195

57. Ethylene, C_2H_4.—Ethylene, or *olefiant gas*, is usually prepared by heating a mixture of sulphuric acid and ethyl alcohol. Ethylsulphuric acid is first formed, which, upon further heating to 165° C. or higher, decomposes into ethylene and sulphuric acid.

Ethylene is also formed by the dry distillation of many organic compounds, and by the action of a boiling alcoholic solution of caustic potash on ethyl bromide, chloride, or iodide; thus,

$$C_2H_5Br+KOH=C_2H_4+KBr+H_2O$$

Ethylene is one of the most important constituents of illuminating gas. It is a colorless gas, with a peculiar sweetish odor, has a specific gravity of .970, is easily condensed to a liquid, and burns with a luminous flame. Mixed with three times its volume of oxygen, it forms an explosive mixture. As it can be liquefied at 10° C. by a pressure of 60 atmospheres, the evaporation of the liquid under reduced pressure affords a valuable means of attaining very low temperatures. Its most characteristic property is its ability to unite directly with other substances, particularly with the halogens, and halogen acids:

$$C_2H_4+Cl_2=C_2H_4Cl_2$$
$$C_2H_4+HCl=C_2H_5Cl$$

The product of ethylene and chlorine has a fragrant odor and is known as *ethylene chloride*, or *Dutch liquid*. Bromine forms a similar compound. Ethylene is readily absorbed by sulphuric acid, forming ethylsulphuric acid.

A mixture of hydrogen and ethylene passed over finely divided nickel at a temperature of about 300° C. is completely converted into ethane.

58. Propylene, $CH_2{:}CH\cdot CH_3$ **and Butylene,** $CH_2{:}CH\cdot C_2H_5$. Propylene and butylene occur in coal gas and in the gases obtained when certain animal and vegetable oils are distilled. Propylene is best prepared by heating allyl iodide with mercury and concentrated hydrochloric acid:

$$C_3H_5I+2Hg+HCl=C_3H_6+HgCl+HgI$$

It is a colorless gas having a feeble, garlic-like odor, boils at −48° C., and is readily absorbed by sulphuric acid. It resembles ethylene closely in all its properties.

Butylene is also a gas that may be condensed to a liquid having a boiling point of 2° C.

ACETYLENE SERIES

59. Structure and Preparation.—The acetylene hydrocarbons correspond to the general formula C_nH_{2n-2}. They are unsaturated hydrocarbons containing two carbon atoms united by triple bonds. The first member of this series is *acetylene*, the second *allylene*, and the higher members are regarded as substituted acetylenes; thus, C_4H_6 is called ethylacetylene, or *butine*.

It has been shown how it is possible to pass from a hydrocarbon of the paraffin series to the corresponding hydrocarbon of the ethylene series by removing hydrogen halide from the halogen compound by heating it with alcoholic potash; thus,

$$C_2H_5Br = C_2H_4 + HBr$$

If this process is continued on the hydrocarbon thus obtained it is possible to obtain a hydrocarbon of the acetylene series, thus,

$$C_2H_4Br_2 = C_2H_2 + 2HBr$$

The acetylenes are also formed by the dry distillation of coal.

60. Acetylene, $CH \equiv CH$.—Acetylene, or *ethine*, is found in small quantities in coal gas. It is the only hydrocarbon that can be obtained by the direct union of its elements. It is formed directly by passing a current of hydrogen between carbon poles heated to incandescence by means of the electric current. Acetylene is also formed by the action of water on alkaline carbides, when coal gas is burned with an insufficient quantity of air, when alcohol, ether, or methane is passed through a red-hot tube, and by treating ethylene bromide with alcoholic caustic potash. Bromoform, chloroform, or iodoform when treated with silver or zinc dust are readily converted into acetylene.

Acetylene is a colorless gas having a disagreeable odor and a specific gravity of .91. It is somewhat soluble in water, and for that reason cannot be collected over water without loss. It burns with a smoky flame, and in the presence of platinum black it unites with hydrogen to form ethylene. Acetylene also unites with nitrogen, in the presence of the electric spark, to form hydrocyanic acid. At a red heat acetylene undergoes polymerization, three molecules of acetylene combining to form one molecule of benzene, C_6H_6. The presence of acetylene in a mixture of gas can be detected by means of the red precipitate of cuprous carbide formed when the gas is passed into an ammoniacal solution of cuprous chloride. When dry, this compound is insoluble in water, is violently explosive at 120° C., and is decomposed by hydrochloric acid, with the evolution of acetylene.

TABLE II
RELATIONSHIP BETWEEN COMPOUNDS

Methane Series	Ethylene Series	Acetylene Series
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
C_2H_6	C_2H_4	C_2H_2
$CH_3 \cdot CH_3$	$CH_2:CH_2$	$CH:CH$
Ethane	Ethylene Ethene	Acetylene Ethine
C_3H_8	C_3H_6	C_3H_4
$CH_3 \cdot CH_2 \cdot CH_3$	$CH_2:CH \cdot CH_3$	$CH:C \cdot CH_3$
Propane	Propylene Propene	Methyl acetylene Allylene Propine
C_4H_{10}	C_4H_8	C_4H_6
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$	$CH_2:CH \cdot CH_2 \cdot CH_3$	$CH:C \cdot C_2H_5$
Butane	Butylene Butene	Ethyl acetylene Butine

Acetylene acts like a weak dibasic acid, forming salts such as *monosodium carbide*, $NaHC_2$; *disodium carbide*, Na_2C_2; *cuprous carbide*, Cu_2C_2; *calcium carbide*, CaC_2; *silver carbide*, Ag_2C_2; etc. Acetylene also unites with bromine, forming tetrabromethane, $C_2H_2Br_4$, and with hydrobromic and hydriodic acids to form substitution products of the saturated hydrocarbons; thus,

$$C_2H_2+2HBr=C_2H_4Br_2$$

61. Allylene, $CH:C \cdot CH_3$.—Only a few of the compounds that succeed acetylene in the series are of importance. *Al-*

lylene, also called methyl acetylene, or propine, is obtained by heating propylene dibromide or dibrompropane, with alcoholic potash; thus,

$$CH_3{\cdot}CHBr{\cdot}CH_2Br+2KOH=CH_3{\cdot}C\vdots CH+2KBr+2H_2O$$

It is a gas very closely resembling acetylene. Its cuprous compound, however, is yellow instead of red.

62. Butine.—Butine, the next member of the series, exists in two isomeric forms, one being *ethyl acetylene*, $C_2H_5{\cdot}C\vdots CH$, and the other, *crotonylene*, or *dimethyl acetylene*, $CH_3{\cdot}C\vdots C{\cdot}CH_3$. The latter does not form metallic derivatives, since this property is possessed only by those compounds which contain the $-C\vdots CH$ group.

63. Relationship Between Compounds.—Before taking up those compounds that have a greater degree of unsaturation than those of the ethylene and acetylene series, it will be of advantage to show by means of Table II the relationship that exists between the saturated hydrocarbons of the methane series and the unsaturated compounds of the ethylene and acetylene series and the different systems of nomenclature used in naming the compounds.

COMPOUNDS OF GREATER UNSATURATION

64. Formation.—Compounds possessing a greater degree of unsaturation than those of the ethylene or acetylene series are known. In the formation of compounds possessing a regularly increasing degree of unsaturation, two hydrogen atoms are always lost in passing from any degree of unsaturation to the next greater. But in the case of the acetylene series, C_nH_{2n-2}, it is obvious that to remove two hydrogen atoms from a hydrocarbon of this type would leave nothing but carbon. Therefore, the only way in which a greater degree of unsaturation can be obtained is to increase the number of double or treble linkings between groups.

65. Diethylenes.—Compounds isomeric with those of the acetylene series but possessing two carbon atoms that are doubly linked instead of one carbon atom that is trebly linked are known. They are called diethylenes or diolefines. The first member of the series is *allene*, $CH_2{:}C{:}CH_2$.

66. Diallyl, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$.—Diallyl, another hydrocarbon of the series, is a liquid having a boiling point of 59° C. It may be prepared by warming allyl iodide, $CH_2{:}CH \cdot CH_2I$, with sodium,

$$2CH_2{:}CH \cdot CH_2I + 2Na = CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2 + 2NaI$$

Diallyl combines with 4 atoms of bromine to form diallyl tetrabromide, $CH_2Br \cdot CHBr \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CH_2Br$.

67. Dipropargyl, $CH{\vdots}C \cdot CH_2 \cdot CH_2 \cdot C{\vdots}CH$.—Dipropargyl is a compound that has two treble linkings. It is formed when diallyl tetrabromide is treated with hot alcoholic potash:

$$CH_2Br \cdot CHBr \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CH_2Br + 4KOH$$
$$= CH{\vdots}C \cdot CH_2 \cdot CH_2 \cdot C{\vdots}CH + 4KBr + 4H_2O$$

DERIVATIVES OF UNSATURATED ALIPHATIC HYDROCARBONS

DERIVATIVES OF ETHYLENE SERIES

MONOHALOGEN SUBSTITUTION PRODUCTS

68. Vinyl Chloride, $CH_2{:}CHCl$.—When chlorine is substituted for one of the hydrogen atoms of ethylene, the gaseous compound vinyl chloride is formed. This compound and the other monohalogen substitution products of ethylene cannot be formed by treating the hydrocarbon with the halogen since saturated addition products such as $CH_2Cl \cdot CH_2Cl$, are formed. In the case of vinyl compounds the substitution is accomplished by treating the halogen addition product with alcoholic potash. Thus,

$$CH_2Cl \cdot CH_2Cl + KOH = CH_2{:}CHCl + KCl + H_2O$$

69. Allyl Chloride, $CH_2{:}CH \cdot CH_2Cl$.—Because of the structure of the second member of the ethylene series, propylene, $CH_2{:}CH{\cdot}CH_3$, it is evident that if a halogen atom is substituted for one of the hydrogen atoms connected to a carbon atom that is doubly linked a different compound will be formed than would be the case if the halogen were substituted for a hydrogen atom connected to a singly linked carbon atom. Thus we have the two propylene chlorides, $CHCl{:}CH{\cdot}CH_3$ and $CH_2{:}CH{\cdot}CH_2Cl$. The first of these when treated with alcoholic potash is converted into a compound of the acetylene series, namely, methyl acetylene.

$$CHCl{:}CH{\cdot}CH_3+KOH=CH{\vdots}C{\cdot}CH_3+KCl+H_2O$$

The second, which is also called allyl chloride, behaves like the monohalogen substitution products of the methane series.

70. As a starting point for the formation of allyl compounds, allyl alcohol, the preparation of which will be given subsequently, is commonly used. Thus, while the monohalogen substitution products may be prepared by the methods already given, they are more easily prepared by treating allyl alcohol with phosphorus and the corresponding halogen.

Allyl chloride is obtained by the distillation of allyl alcohol with phosphorus trichloride, as well as by the method already given. It is a colorless liquid with a pungent odor, is insoluble in water, boils at 46° C., and has a specific gravity of .937. Allyl iodide is the reaction product of phosphorus, iodine, and allyl alcohol. Allyl triiodide is first formed but readily decomposes into allyl iodide and iodine. It is a yellowish liquid with a strong odor, boils at 103° C., is soluble in alcohol, and has a specific gravity of 1.785.

71. Allyl Bromide, $CH_2{:}CH{\cdot}CH_2Br$.—Allyl bromide is obtained when allyl alcohol is treated with phosphorus and bromine. Phosphorus tribromide, PBr_3, is first formed, which reacts with the alcohol to form the halogen compound

$$3CH_2{:}CH{\cdot}CH_2{\cdot}OH+PBr_3=3CH_2{:}CH{\cdot}CH_2Br+H_3PO_3$$

Allyl bromide is a colorless liquid with a pungent odor. It boils at 70° C., has a specific gravity of 1.436 and is soluble in alcohol and ether.

72. Allyl Sulphide, $(CH_2{:}CH{\cdot}CH_2)_2S$.—Allyl sulphide, the chief constituent of oil of garlic, is obtained by the distillation of garlic with water. It is prepared synthetically by the treatment of allyl iodide with potassium sulphide:

$$2C_3H_5I+K_2S=(C_3H_5)_2S+2KI$$

It is a colorless, oily liquid with a disagreeable odor; it is soluble in alcohol, only slightly soluble in water, and boils at 138° C.

CYANOGEN SUBSTITUTION PRODUCTS

73. Allyl Cyanides.—Since the allyl halides react in the same manner as the monohalogen substitution products of the methane series, the allyl cyanides may be prepared by methods similar to those for the preparation of the alkyl cyanides.

74. Allyl Isothiocyanate, $CH_2{:}CH{\cdot}CH_2{\cdot}NCS$.—Allyl isothiocyanate, also known as allyl mustard oil, or simply mustard oil, occurs naturally in black mustard seed and may be obtained by macerating and distilling them. It is synthetically prepared by heating allyl iodide with potassium thiocyanate. Allyl thiocyanate is first formed,

$$CH_2{:}CH{\cdot}CH_2I+KSCN=CH_2{:}CH{\cdot}CH_2SCN+KI$$

This compound is then converted into allyl isothiocyanate by heat. Pure allyl isothiocyanate is a colorless or pale-yellow liquid with a very pungent odor and an acrid, burning taste. It is only slightly soluble in water, boils at 150.7° C., and has a specific gravity of 1.018. It causes blisters on the skin.

When heated with water or hydrochloric acid or with zinc and hydrochloric acid, it is converted into allyl amine, showing that in it the allyl radical is in combination with nitrogen and not with sulphur.

ALCOHOLS

75. Derivation and Structure.—The unsaturated alcohols are derived from the unsaturated hydrocarbons in the same manner as the saturated alcohols are derived from the saturated hydrocarbons. Their general formula is $C_nH_{2n-1}OH$.

In addition to possessing the general characteristics of the saturated alcohols, they also have the property of combining directly with two additional atoms or groups. The hydroxl group of these alcohols may be attached either to a singly linked or a doubly linked carbon atom, forming primary or secondary alcohols:

$CH_2{:}CH{\cdot}CH_2OH$	$CH_2{:}CH{\cdot}OH$
primary	secondary
(allyl alcohol)	(vinyl alcohol)

Primary alcohols contain the group CH_2OH. Therefore, it is evident that the first member of the series, which is derived from ethylene, $CH_2{:}CH_2$, will not be a primary but a secondary alcohol.

76. Vinyl Alcohol, $CH_2{:}CHOH$.—Aside from its preparation from ethylene, vinyl alcohol may also be obtained by the oxidation of ether; thus,

$$C_2H_5{\cdot}O{\cdot}C_2H_5+O_2=2CH_2{:}CHOH+H_2O$$

It is also formed when ether is exposed to the combined action of air and sunlight.

77. Allyl Alcohol, $CH_2{:}CH{\cdot}CH_2OH$.—The most important representative of the unsaturated alcohols of the ethylene series is allyl alcohol. It is prepared by the following methods:

1. By treating allyl iodide with silver hydroxide,

$$CH_2{:}CH{\cdot}CH_2I+AgOH=CH_2{:}CH{\cdot}CH_2OH+AgI$$

2. By treating glycerol, $C_3H_5(OH)_3$, with phosphorus triiodide,

Allyl iodide is first formed,

$$C_3H_5(OH)_3+PI_3=CH_2{:}CH{\cdot}CH_2I+H_3PO_3+I_2$$

which upon being heated to 100° C., with water breaks up into allyl alcohol and hydriodic acid; thus,

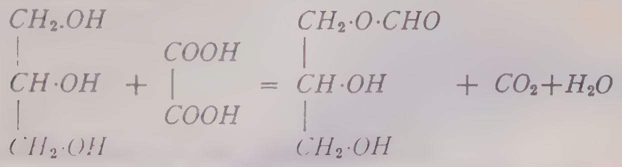
$$CH_2{:}CH{\cdot}CH_2I+H_2O=CH_2{:}CH{\cdot}CH_2OH+HI$$

3. From glycerol, by treating dichlorhydrin with sodium,

$$C_3H_5(OH)_3+2HCl=\underset{\text{dichlorhydrin}}{C_3H_5Cl_2{\cdot}OH}+2H_2O$$

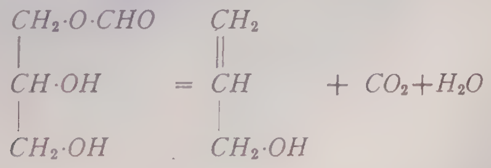
$$C_3H_5Cl_2OH+2Na=CH_2{:}CH{\cdot}CH_2OH+2H_2O$$

4. It is best obtained by heating glycerol with formic or oxalic acid. The glycerol is heated with one-fourth of its weight of oxalic acid in a retort at about 195° C., as long as water distils over. Afterwards the temperature is raised to 225° C., when the allyl alcohol distils over. In this method formic acid is obtained from the breaking down of the oxalic acid, and this unites with the glycerol, producing monoformin; thus,



$$\begin{array}{l} CH_2.OH \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array} + \begin{array}{l} COOH \\ | \\ COOH \end{array} = \begin{array}{l} CH_2{\cdot}O{\cdot}CHO \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array} + CO_2 + H_2O$$

The monoformin then decomposes into allyl alcohol, carbon dioxide, and water:



$$\begin{array}{l} CH_2{\cdot}O{\cdot}CHO \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array} = \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2{\cdot}OH \end{array} + CO_2 + H_2O$$

78. Allyl alcohol is a colorless liquid with a pungent, suffocating, characteristic odor. It boils at 96° C., and has a specific gravity of .865. It solidifies at −50° C., and is miscible with water in all proportions. Allyl alcohol forms esters with acids, and when treated with potassium permanganate yields glycerol. It is a primary alcohol, as is shown by the fact that it is converted into an aldehyde (acrolein, $CH_2{:}CH{\cdot}CHO$) and an acid (acrylic acid, $CH_2{:}CH{\cdot}COOH$) by oxidizing agents.

ALDEHYDES

79. General Properties.—The aldehydes of the olefine series bear the same relation to the alcohols of the series that the saturated aldehydes do to the saturated alcohols. While the aldehyde group has the same reactive properties as in the ordinary aldehydes, the double bond in the olefine aldehydes modifies somewhat their aldehydic character. The difference due to the double bond is shown in their behavior toward ammonia. Acetaldehyde unites directly with ammonia; thus,

$$C_2H_4O+NH_3=C_2H_4ONH_3$$

while acrylic aldehyde, the first member of this series, unites according to the equation

$$2C_3H_4O+NH_3=C_6H_9ON+H_2O$$

In addition to the regular reactions, the unsaturated residue C_nH_{2n-2} has the property of forming addition products similar to those of the olefines, and, further, some of the olefine aldehydes are connected with the saturated aldehydes by condensation reactions, as, for example, crotonaldehyde, or crotonic aldehyde.

Of these aldehydes the only important ones that need be treated are acrylic aldehyde and crotonic aldehyde.

80. Acrylic Aldehyde, $CH_2{:}CH{\cdot}CHO$.—Acrylic aldehyde, or acrolein is prepared by distilling impure glycerine or fats with potassium hydrogen sulphate. It is also produced by the oxidation of allyl alcohol. It is always produced when the ordinary fats are heated to high temperatures, and the peculiar pungent odor noticed when this occurs, or when a tallow candle or oil lamp is extinguished, is due to the formation of acrolein.

Acrolein is a colorless, volatile liquid, boiling at 52.4° C., and having a specific gravity of .841. It is only slightly soluble in water, but dissolves readily in alcohol and ether. It has a pungent penetrating odor, and its vapor acts violently on the mucous membrane of the eyes, causing the secretion of tears.

On oxidation, acrolein passes into acrylic acid, and nascent hydrogen reduces it to allyl alcohol. It does not combine with the alkali acid sulphates, but forms a resinous body with the hydroxides of potassium and sodium. It reduces an ammoniacal solution of silver nitrate, forming a mirror-like deposit. By careful preservation, acrolein forms, after a time, an amorphous white solid, known as disacryl, which, while seemingly polymeric with acrolein, cannot be reconverted into the original substance.

81. Crotonic Aldehyde, $CH_3{\cdot}CH{:}CH{\cdot}CHO$.—Crotonic aldehyde, or crotonaldehyde, is formed when acetaldehyde is heated with dilute hydrochloric acid or with water and zinc chloride. Neither the acid, the water, nor the zinc chloride takes any part in the reaction except to form the compound aldol, which in turn gives up one molecule of water and yields the crotonic aldehyde, according to the equation

$$CH_3{\cdot}CHOH{\cdot}CH_2{\cdot}CHO = CH_3{\cdot}CH{:}CH{\cdot}CHO + H_2O$$

Crotonic aldehyde is a liquid with an irritating odor; it boils at 104° C. and has a specific gravity of 1.033. It is only slightly soluble in water. Moist silver oxide readily oxidizes it to crotonic acid.

ACIDS

82. Preparation, Properties, and Structure.—The acids of the olefine series, called the *oleic series*, bear the same relation to the ethylene series of hydrocarbons that the fatty acids bear to the saturated hydrocarbons. They differ from the fatty acids in that they contain two atoms less of hydrogen. They have the general formula $C_nH_{2n-2}O_2$.

These acids can be prepared from unsaturated compounds by the oxidation of the unsaturated alcohols and aldehydes, and by the conversion of unsaturated halogen compounds into the cyanide and the further conversion of this compound into the acid. They are prepared from saturated acids by the action of alcoholic potash on the monohalogen derivative of the saturated acid, and by the removal of water from the monohydroxy acids.

Like other unsaturated compounds, the acids of the olefine series contain a double bond, and hence possess the property of forming addition products. They are stronger acids than the fatty acids, containing the same number of carbon atoms in the molecule. They are more readily oxidized owing to the double bond, and are converted into two saturated acids by strong oxidizing agents. The action of less energetic oxidizing agents forms a dihydroxy acid, which, on further oxidation, breaks the chain at the double bond. Only a few of the unsaturated acids are of sufficient importance to be considered.

83. Acrylic Acid, $CH_2{:}CH{\cdot}COOH$.—Acrylic acid may be prepared by treating β-iodopropionic acid with alcoholic caustic potash; thus:

$$CH_2I{\cdot}CH_2{\cdot}COOH+KOH=CH_2{:}CH{\cdot}COOH+KI+H_2O$$

It is best made, however, by oxidizing acrolein with silver oxide.

Acrylic acid is a liquid having a very pungent odor like that of acetic acid. It boils at 140° C., and solidifies at 7° C. Nascent hydrogen reduces it to propionic acid.

Acrylic acid forms salts with the metals; these salts, with the exception of the silver salt, are soluble in water.

84. Crotonic Acid, $CH_3{\cdot}CH{:}CH{\cdot}COOH$.—Crotonic acid exists in several isomeric modifications, only one of which, solid crotonic acid, will be considered.

Solid crotonic acid is best prepared by the oxidation of crotonic aldehyde with silver oxide:

$$CH_3{\cdot}CH{:}CH{\cdot}CHO \rightarrow CH_3{\cdot}CH{:}CH{\cdot}COOH$$

It is also prepared by distilling β-hydroxybutyric acid; thus,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}COOH=CH_3{\cdot}CH{:}CH{\cdot}COOH+H_2O$$

As crotonic acid occurs in crude pyroligneous acid, it is frequently obtained from this source. It crystallizes in slender needles or in plates, melts at 72° C., and boils at 185° C. It is soluble in water. When fused with caustic potash it yields acetic acid. Its aqueous solutions, when boiled with an alkaline silver solution, reduces the solution, forming a silver mirror. Nitric acid oxidizes solid crotonic acid to acetic and oxalic acids. Nascent hydrogen reduces it to butyric acid.

85. Oleic Acid, $C_{17}H_{33}COOH$.—Oleic acid is the most important of the ethylene series of acids. It is found as an ester of glycerol, $C_3H_5(OH)_3$, in fats and oils. It is obtained whenever the fat or oil is subjected to the action of saponifying agents such as caustic soda.

At ordinary temperatures oleic acid is a clear, colorless oily liquid that solidifies at 0° C. to a white granular mass, and melts at 14° C. It is insoluble in water, but soluble in alcohol, ether, and fixed and volatile oils. Its specific gravity is .898. In a pure condition oleic acid is odorless and has no effect on litmus paper, but on exposure to the air it oxidizes, becomes yellow in color, and acquires a rancid odor. It cannot be distilled at ordinary pressures without suffering decomposition, although it can be distilled in a current of superheated steam at 250° C. without decomposing. Hydriodic acid reduces oleic acid to stearic acid, thus showing the presence of a normal carbon chain.

86. The presence of a double bond in oleic acid is shown by its forming an addition product with bromine, namely, dibromstearic acid. This is also shown by its ability to reduce an alkaline permanganate solution. Careful oxidation of oleic acid yields pelargonic acid, $C_8H_{17}\cdot COOH$, and azelaic acid, $COOH\cdot(CH_2)_7\cdot COOH$, indicating that the double bond is situated at the center of the chain, and that the constitutional formula of oleic acid is $CH_3\cdot(CH_2)_7\cdot CH{:}CH\cdot(CH_2)_7\cdot COOH$.

Oleic acid readily reacts with nitrous acid, to form a crystalline isomeride, *elaidic acid*. This reaction is known as the *elaidic transformation*. In the presence of finely divided nickel, which acts as a catalyser, oleic acid reacts with hydrogen to form stearic acid. Thus,

$$C_{17}H_{33}COOH+2H=C_{17}H_{35}COOH$$

87. The alkali salts of oleic acid, known as *oleates*, are easily decomposed, an excess of water forming the free alkali and insoluble acid oleates. *Sodium oleate*, $C_{17}H_{33}COONa$, is always present in ordinary soap and may be crystallized from absolute alcohol in the form of yellow, fatty granules soluble in water. *Barium oleate*, $(C_{17}H_{33}COO)_2Ba$, is obtained as a white, granular mass soluble in alcohol and ether, but insoluble in water. *Lead oleate*, $(C_{17}H_{33}COO)_2Pb$, is the reaction product between sodium oleate and lead acetate. It forms white granules soluble in alcohol, ether, and oil of turpentine, fuses at 80° C., and solidifies on cooling to a white, translucent, brittle mass. This salt is used in lacquers.

DERIVATIVES OF ACETYLENE SERIES

ALCOHOLS

88. Propargyl Alcohol, $CH{\vdots}C{\cdot}CH_2{\cdot}OH$.—Propargyl alcohol is the only well-known member of the series. It contains a pair of trebly linked carbon atoms and is the hydroxyl derivative of allylene or methyl acetylene. It is formed when bromallyl alcohol is treated with alcoholic potash:

$$CH_2{:}CBr{\cdot}CH_2OH + KOH = CH{\vdots}C{\cdot}CH_2OH + KBr + H_2O$$

The presence of the group $\equiv CH$ is shown by its ability to form metallic derivatives. Its silver salt, $C_3H_2(OH)Ag$, is white in color and very explosive.

89. Properties.—Propargyl alcohol is a mobile liquid with an agreeable odor, it is soluble in water, burns with a luminous flame, boils at 115° C., and has a specific gravity of .963.

ACIDS

90. Propiolic Acid, $CH{\vdots}C{\cdot}COOH$.—Propiolic acid is formed by the action of carbon dioxide on the sodium compounds of the acetylene hydrocarbons. It is also formed by the action of alcoholic potash on the bromine addition products of the acids of the oleic-acid series.

Propiolic acid is a liquid with an odor resembling that of acetic acid. It solidifies at 6° C., and boils at 144° C., undergoing decomposition. It forms explosive metallic derivatives. Prolonged boiling of an aqueous solution of the potassium salt decomposes it into acetylene and potassium carbonate. The acid is readily soluble in water and alcohol, reduces silver and platinum salts, and is reduced to propionic acid by means of sodium amalgam.

91. Linoleic Acid, $C_{17}H_{31}{\cdot}COOH$.—Linoleic acid occurs as a glyceride in drying oils. It is obtained by the saponification of linseed oil, hemp oil, or poppy oil. One of the most characteristic properties of linoleic acid is its ready absorption of oxygen from the air, forming a solid substance. This acid also contains two double bonds, as is proved by a careful oxidation with permanganate, when tetrahydroxystearic acid is formed.

GENERAL DISCUSSION OF UNSATURATED HYDROCARBONS AND DERIVATIVES

92. All of the unsaturated hydrocarbons and their derivatives that have been considered, are obtainable from the saturated hydrocarbons by means of simple reactions. All have the property of taking up halogens or halogen acids, thus passing back to the saturated condition. Although the real nature of the relation existing between the carbon atoms of the unsaturated hydrocarbons may not be clearly defined, it is easily changed to the relation existing in the saturated compounds.

93. The hydrocarbons already treated group themselves under three general heads in the order of their prominence, and the number of their derivatives. These groups are:

1. Hydrocarbons C_nH_{2n+2} and derivatives.
2. Hydrocarbons C_nH_{2n} and derivatives.
3. Hydrocarbons C_nH_{2n-2} and derivatives.

The compounds of the first group, or the paraffins, are by far the most important as well as the most numerous. The compounds of the second group, the olefines, are neither so numerous nor are very many of them familiar substances. Of the third group, or acetylenes, only a very few of the hydrocarbons or derivatives are known, and our knowledge of them is more limited than of those of the second group. Very little is known about the hydrocarbons possessing still a greater degree of unsaturation than those of the three preceding groups.

POLYSUBSTITUTION PRODUCTS OF SATURATED ALIPHATIC HYDROCARBONS

DISUBSTITUTION PRODUCTS AND DERIVATIVES

DIHALOGEN COMPOUNDS

94. The products formed by the treatment of ethane and ethylene with chlorine have been discussed. Thus it has been shown that starting with either ethane or ethylene, it is possible to form the compound $C_2H_4Cl_2$. It has also been stated that only the symmetrical compound $CH_2Cl \cdot CH_2Cl$, or ethylene chloride is formed when chlorine is added to ethylene. The symmetrical dihalogens thus obtained are very important from the standpoint of synthetic organic chemistry. They are easily acted upon by such reagents as caustic potash, potassium cyanide, and ammonia to form symmetrical disubstitution products of ethane.

Another important reaction of the dihalogen ethylenes is based upon the facility with which they are acted upon by an alcoholic potash solution to form vinyl compounds. In this reaction a saturated compound $CH_2Cl \cdot CH_2Cl$, for instance, is acted upon and forms the unsaturated vinyl chloride or monochlorethylene, $CH_2{:}CHCl$. Vinyl chloride, in turn, may be treated with chlorine and trichlorethane formed. Thus,

$$CH_2{:}CHCl + Cl_2 = CH_2Cl \cdot CHCl_2$$

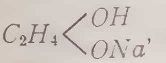
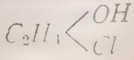
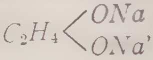
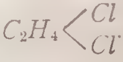
In this manner, starting with dichlorethane, hexachlorethane may be prepared.

DIHYDROXY ALCOHOLS OR GLYCOLS

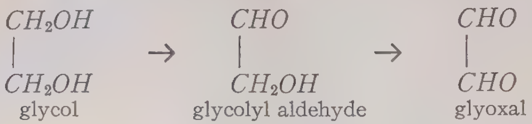
95. Formation.—The dihydroxy alcohols, or glycols, may be regarded as being obtained from the saturated hydrocarbons, by the substitution of two hydroxyl radicals for two hydrogen atoms attached to two different carbon atoms. An assumption of their formation is expressed by their nomenclature, ethylene glycol, propylene glycol, namely, that they are olefine compounds combined with two hydroxyl groups. The glycols were first discovered by Wurtz, in 1854, and were so named because of filling the gap between the mono-hydroxy alcohols and the tri-hydroxy alcohol, glycerol. They are formed, as a whole, by combining an olefine with bromine and then heating the compound thus formed with an alcoholic solution of potassium acetate. This forms a diacetate of the olefine which, in turn, is decomposed with caustic potash, forming a dihydroxy alcohol and potassium acetate, the former being distilled off.

96. General Properties of Glycols.—In the case of the mono-hydroxy alcohols, three classes were noticed: primary, secondary, and tertiary. The classes of glycols are twice as numerous: diprimary, secondary primary, disecondary, ditertiary, or pinacones, secondary tertiary, and primary tertiary.

The simplest member of the dihydroxy alcohols would naturally be $CH_2(OH)_2$, from methane, but this compound has never been isolated. No compound seems to exist that has two hydroxyl groups linked to one carbon atom. Many compounds containing several hydroxyl groups are known, but none has more than one hydroxyl group in combination with each carbon atom.

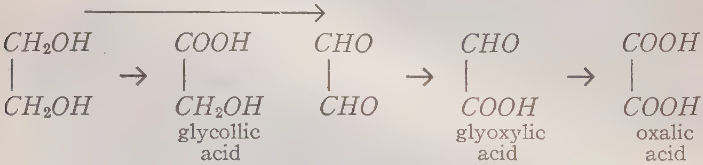
The hydroxyl groups in the glycols can be transformed the same as the corresponding group in the monohydroxy alcohols. The hydrogen in them can be replaced by alkali metals, forming glycolates, and the groups can be exchanged for acid radicals, etc. As there are two hydroxyl groups in the glycols, there are two series of substituted glycols, namely, one series in which only one hydroxyl group is changed, as sodium glycollate,  $C_2H_4<\genfrac{}{}{0pt}{}{OH}{ONa}$, or glycol chlorhydrin,  $C_2H_4<\genfrac{}{}{0pt}{}{OH}{Cl}$, and another in which both hydroxyl groups are replaced as disodium glycollate,  $C_2H_4<\genfrac{}{}{0pt}{}{ONa}{ONa}$, or ethylene chloride,  $C_2H_4<\genfrac{}{}{0pt}{}{Cl}{Cl}$.

97. On oxidation, the glycols yield the same products as are obtained by the oxidation of the alcohols; and as there are two alcohol groups to be oxidized, an extremely large number of products are obtained. Both alcohol groups can be oxidized to aldehyde groups, or only one may be so treated; for example,



$$\underset{\text{glycol}}{\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}} \rightarrow \underset{\text{glycolyl aldehyde}}{\begin{array}{l}CHO\\ |\\ CH_2OH\end{array}} \rightarrow \underset{\text{glyoxal}}{\begin{array}{l}CHO\\ |\\ CHO\end{array}}$$

or one or both may be oxidized to acid groups, forming *alcohol acids*, *aldehyde acids*, or *acids*; for example,



$$\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array} \rightarrow \underset{\text{glycollic acid}}{\begin{array}{l}COOH\\ |\\ CH_2OH\end{array}} \overset{\longrightarrow}{} \begin{array}{l}CHO\\ |\\ CHO\end{array} \rightarrow \underset{\text{glyoxylic acid}}{\begin{array}{l}CHO\\ |\\ COOH\end{array}} \rightarrow \underset{\text{oxalic acid}}{\begin{array}{l}COOH\\ |\\ COOH\end{array}}$$

If the glycol contains the secondary alcohol group, $CHOH$, ketone alcohols, ketone aldehydes, ketone acids, and diketones can be prepared. Hence, the glycols give rise to a very large number of derivatives, many of which are very important although the glycols themselves are not so very important.

98. Ethylene Glycol, $CH_2OH \cdot CH_2OH$.—Ethylene glycol was discovered in 1854 by Würtz. It may be prepared by starting with ethylene and forming ethylene bromide by the direct addition of bromine. This product is then treated with silver acetate, when the following reaction takes place:

$$\underset{\text{ethylene bromide}}{C_2H_4Br_2}+\underset{\text{silver acetate}}{2CH_3COOAg}=\underset{\text{silver bromide}}{2AgBr}+\underset{\text{ethylene diacetate}}{(CH_3COO)_2C_2H_4}$$

The ethylene diacetate is then subjected to saponification with caustic potash, ethylene glycol being formed.

$$(CH_3COO)_2C_2H_4+2KOH=\underset{\text{potassium acetate}}{2CH_3COOK}+\underset{\text{ethylene glycol}}{C_2H_4(OH)_2}$$

Another method of formation is to decompose with moist silver oxide, the chlorhydrin, obtained by treating ethylene with hypochlorous acid. This method is illustrated by the equations,

$$C_2H_4+HClO=\underset{\text{ethylene chlorhydrin}}{C_2H_4\cdot ClOH}$$

$$2C_2H_4\cdot ClOH+Ag_2O+H_2O=2C_2H_4(OH)_2+2AgCl$$

A third method is to oxidize an alkaline solution of ethylene with either potassium permanganate or hydrogen peroxide. This method is illustrated by the equation,

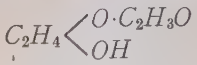
$$C_2H_4+O+H_2O=C_2H_4(OH)_2$$

99. Ethylene glycol is best prepared in the laboratory, however, by decomposing ethylene bromide with potassium carbonate. In this method, ethylene, prepared from alcohol and sulphuric acid, is converted into ethylene bromide by passing it slowly into 50 grams of bromine under water, well cooled, until the bromine is nearly or quite bleached. The heavy layer of ethylene bromide is shaken with a little weak caustic-potash solution and the upper layer removed. Fifty grams of the ethylene bromide is now heated with 40 grams of potassium carbonate and 100 cubic centimeters of water for about 16 to 18 hours in a flask connected with an upright or reflux condenser. When the ethylene bromide no longer condenses and runs back, the condenser is placed in the usual position, and the contents of the flask are distilled. After all the water has distilled over, the receiver is changed and the flask is strongly heated when the glycol distils over. The reaction for this method is illustrated by the equation

$$C_2H_4Br_2+K_2CO_3+H_2O=C_2H_4(OH)_2+2KBr+CO_2$$

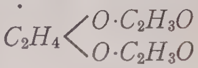
100. Properties of Ethylene Glycol.—Ethylene glycol is a colorless, sirupy liquid with a sweet taste and a specific gravity of 1.004 at 20° C., and is inodorous. It is soluble in all proportions of water and alcohol, but only slightly soluble in ether. Ethylene glycol boils at 197° C. and distils without decomposition.

In its conduct toward acids, ethylene glycol acts as a diacid base and forms neutral and alcoholic salts. The acetates are very good examples of this, the monoacetate corresponding to a basic salt, and the diacetate to a neutral compound; thus



$$C_2H_4\left\langle\begin{array}{l}O\cdot C_2H_3O\\OH\end{array}\right.$$

monoacetate

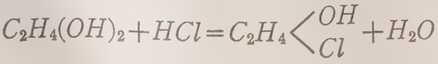


$$C_2H_4\left\langle\begin{array}{l}O\cdot C_2H_3O\\O\cdot C_2H_3O\end{array}\right.$$

diacetate

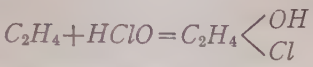
101. Structure of Ethylene Glycol.—The structure of ethylene glycol may be represented by either $\begin{array}{l}CH_2\cdot OH\\|\\CH_2\cdot OH\end{array}$ or $\begin{array}{l}CH\cdot(OH)_2\\|\\CH_3\end{array}$. In one formula the hydroxyl is in combination with different carbon atoms and in the other both hydroxyl groups are in combination with the same carbon atom. The question arising as to which formula ethylene alcohol corresponds is decided as follows: Ethylene chloride corresponds to the formula $\begin{array}{l}CH_2Cl\\|\\CH_2Cl\end{array}$, and it is known that when the chlorine atoms are replaced with hydroxyl, ethylene alcohol is formed. Ethylidene chloride, $\begin{array}{l}CHCl_2\\|\\CH_3\end{array}$, is formed from aldehyde by replacing the oxygen of the aldehyde group with two chlorine atoms. Hence, ethylene alcohol has each hydroxyl group in combination with a different carbon atom. All attempts to prepare the dihydroxy alcohol corresponding to ethylidene chloride, with both hydroxyls in combination with the same carbon atom, have failed. Instead of obtaining ethylidene alcohol, aldehyde is almost invariably formed. These facts prove the statement that compounds having more than one hydroxyl group attached to the same carbon atom do not exist or are very unstable.

102. Ethylene Chlorohydrin, $C_2H_4OH\cdot Cl$.—Ethylene chlorohydrin or glycol chlorohydrin is formed when hydrochloric-acid gas is passed into ethylene glycol; thus,



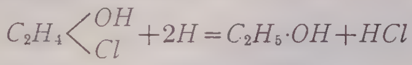
$$C_2H_4(OH)_2+HCl=C_2H_4\left\langle\begin{array}{l}OH\\Cl\end{array}\right.+H_2O$$

It is made on a commercial scale by heating glycol with sulphur monochloride. It can also be prepared by the combination of ethylene with hypochlorous acid, as is shown by the equation



$$C_2H_4+HClO=C_2H_4\left\langle\begin{matrix}OH\\Cl\end{matrix}\right.$$

This compound permits the conversion of a dihydroxy alcohol to a monohydroxy alcohol yielding ethyl alcohol when acted on by nascent hydrogen, as is shown by the equation

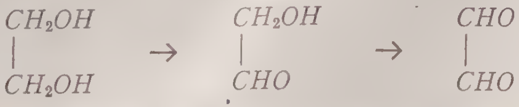


$$C_2H_4\left\langle\begin{matrix}OH\\Cl\end{matrix}\right.+2H=C_2H_5\cdot OH+HCl$$

Ethylene chlorohydrin is a colorless liquid with a specific gravity of 1.223; it is soluble in all proportions of water and boils at 128° C. When oxidized it yields monochloracetic acid, $CH_2Cl\cdot COOH$, from which it is obvious that the chlorine cannot be attached to the same carbon atom as that to which the oxygen and hydroxyl are attached, for if it were, the substance would not be an acid. This proves that the chlorine and hydroxyl of ethylene chlorohydrin must be attached to different carbon atoms and thus furnishes further proof of the constitution of ethylene glycol.

DIALDEHYDES

103. Glyoxal, $CHO\cdot CHO$.—Glyoxal, or oxalic aldehyde, is the final product of the careful oxidation of ethylene glycol. The reaction may be shown thus:

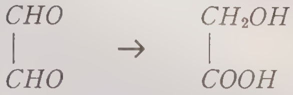


$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}\rightarrow\begin{matrix}CH_2OH\\|\\CHO\end{matrix}\rightarrow\begin{matrix}CHO\\|\\CHO\end{matrix}$$

It is best prepared by floating a layer of water on strong nitric acid in a tall glass cylinder, and pouring ethyl alcohol on the surface of the water, taking care that the layers do not mix immediately. Slow oxidation of the alcohol to acetaldehyde and then to glyoxal takes place under these conditions.

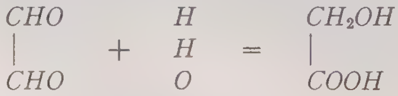
104. Properties.—The glyoxal thus prepared is a colorless, deliquescent, amorphous solid that is very soluble in water and alcohol when moist, but which dissolves very slowly after completely drying at 110° C. It is a polymeride of unknown molecular weight. Distilled with phosphoric anhydride, an emerald-colored gas is evolved, which condenses to beautiful yellow crystals. These melt at 15° C. to a yellow liquid that boils at 51° C. In this form it is monomolecular glyoxal and is rather unstable, as traces of water readily polymerize it.

Glyoxal combines with two molecules of sodium hydrogen sulphite, thus proving it to be a dialdehyde. Like other aldehydes, it reduces an ammoniacal solution of silver nitrate with the formation of a mirror. Alkalies convert it into glycollic acid, one aldehyde group being reduced and the other oxidized, thus,



$$\begin{array}{c} CHO \\ | \\ CHO \end{array} \rightarrow \begin{array}{c} CH_2OH \\ | \\ COOH \end{array}$$

This reaction is probably explained by the assumption that an addition product with water is formed; thus,



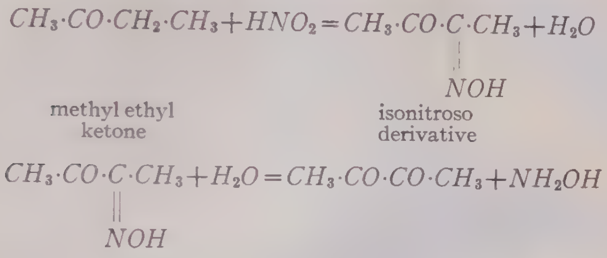
$$\begin{array}{c} CHO \\ | \\ CHO \end{array} + \begin{array}{c} H \\ H \\ O \end{array} = \begin{array}{c} CH_2OH \\ | \\ COOH \end{array}$$

DIKETONES

105. Structure and Nomenclature.—The ketones already studied contained only one carbonyl group. Some ketones, however, contain two carbonyl groups and are therefore termed *diketones*. The members of the series are named according to the positions occupied by the carbonyl groups. The following formulas illustrate the nomenclatures used:

$R{\cdot}\overset{1}{CO}{\cdot}\overset{2}{CO}{\cdot}R$	Alpha diketones or 1–2 diketones
$R{\cdot}\overset{1}{CO}{\cdot}\overset{2}{CH_2}{:}\overset{3}{CO}{\cdot}R$	Beta diketones or 1–3 diketones
$R{\cdot}\overset{1}{CO}{\cdot}\overset{2}{CH_2}{\cdot}\overset{3}{CH_2}{\cdot}\overset{4}{CO}{\cdot}R$	Gamma diketones or 1–4 diketones

106. Diacetyl, $CH_3\cdot CO\cdot CO\cdot CH_3$.—Diacetyl is formed by the action of nitrous acid on methyl ethyl ketone and the subsequent hydrolysis of the intermediate compound formed.



$$CH_3\cdot CO\cdot CH_2\cdot CH_3+HNO_2=CH_3\cdot CO\cdot \underset{\underset{NOH}{\|}}{C}\cdot CH_3+H_2O$$

$$CH_3\cdot CO\cdot \underset{\underset{NOH}{\|}}{C}\cdot CH_3+H_2O=CH_3\cdot CO\cdot CO\cdot CH_3+NH_2OH$$

Diacetyl is a yellow liquid, soluble in water, and possessing a sweet but pungent odor. It has a specific gravity of .9734 at 22° C., and boils at 87.5° C.

TRISUBSTITUTION PRODUCTS AND DERIVATIVES

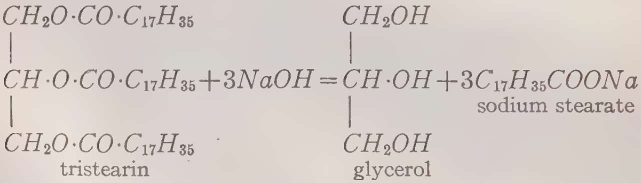
TRIHYDROXY ALCOHOLS

107. Composition and Structure.—The trihydroxy alcohols may be regarded as being derived from saturated hydrocarbons by the substitution of three hydroxyl groups for three atoms of hydrogen. As only one hydroxyl can remain combined with an atom of carbon, the simplest trihydroxy alcohol must contain three atoms of carbon, hence, $C_3H_5(OH)_3$ must be the lowest member of this group. The trihydroxy alcohols are all known as glycerols from the first and most important member. The number of known glycerols is rather limited, but what has been said with regard to isomerism, substitution derivatives, and oxidation products of the glycols applies with even greater force to the glycerols, in which there are three hydroxyl groups to be replaced and three alcohol groups to be oxidized.

108. Glycerol, $C_3H_5(OH)_3$.—Glycerol, or glycerine, as it is frequently called, was discovered by Scheele in 1779, and later

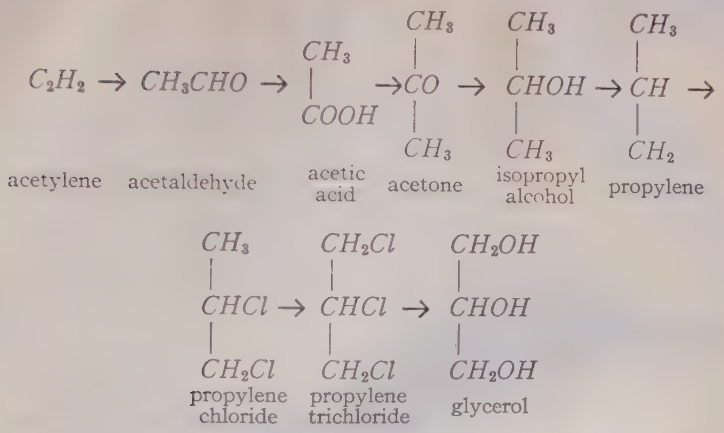
Berthelot, in conjunction with Lucca and Würtz, explained its constitution and proved it to be the simplest trihydroxy alcohol. It is produced in small quantities in the alcoholic fermentation of sugar; hence, it is found in wines. It also occurs as the glycerol ester of fatty acids in the fats and oils from which it is prepared. The esters of the fatty acids are named according to the acids from which they are formed. Thus the ester, or glyceride, formed from acetic acid is called *triacetin;* that from palmitic acid, *tripalmitin;* and that from stearic acid, *tristearin.*

When fats or oils are saponified by treatment with a caustic alkali, superheated steam, or other saponifying agents, the esters or glycerides of the fatty acids that they contain are split up, glycerol being set free with the formation of the fatty acid or its salt when an alkali is used as the saponifying agent. Thus,



$$\begin{array}{lcl}
CH_2O\cdot CO\cdot C_{17}H_{35} & & CH_2OH \\
| & & | \\
CH\cdot O\cdot CO\cdot C_{17}H_{35}+3NaOH & = & CH\cdot OH+3C_{17}H_{35}COONa \\
| & & | \qquad\qquad\qquad \text{sodium stearate} \\
CH_2O\cdot CO\cdot C_{17}H_{35} & & CH_2OH \\
\text{tristearin} & & \text{glycerol}
\end{array}$$

109. Glycerol may be prepared synthetically in the laboratory, starting with acetylene gas. The method is of theoretical interest only. In the process acetylene is converted into acetaldehyde by treatment with mercuric bromide and dilute sulphuric acid. The aldehyde is then oxidized to acetic acid from which calcium acetate is next formed and which is then converted into acetone. The acetone, when reduced, passes into isopropyl alcohol, which is then treated with anhydrous zinc chloride, withdrawing the water from it and forming propylene. Chlorine is now added to the propylene, forming propylene chloride, while the addition of iodine chloride to propylene chloride forms propenyl trichloride. When propenyl trichloride or trichlorohydrin is heated to 160° C. with a large quantity of water glycerol is produced. The various steps in this process are as follows:



$$\underset{\text{acetylene}}{C_2H_2} \rightarrow \underset{\text{acetaldehyde}}{CH_3CHO} \rightarrow \underset{\text{acetic acid}}{\begin{array}{l} CH_3 \\ | \\ COOH \end{array}} \rightarrow \underset{\text{acetone}}{\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}} \rightarrow \underset{\text{isopropyl alcohol}}{\begin{array}{c} CH_3 \\ | \\ CHOH \\ | \\ CH_3 \end{array}} \rightarrow \underset{\text{propylene}}{\begin{array}{c} CH_3 \\ | \\ CH \\ | \\ CH_2 \end{array}} \rightarrow$$

$$\underset{\text{propylene chloride}}{\begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}} \rightarrow \underset{\text{propylene trichloride}}{\begin{array}{l} CH_2Cl \\ | \\ CHCl \\ | \\ CH_2Cl \end{array}} \rightarrow \underset{\text{glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}}$$

Large quantities of glycerol are recovered in the manufacture of soaps.

110. Structure of Glycerol.—According to the rule that two hydroxyl groups cannot be attached to the same carbon atom, the structure of glycerol must be $CH_2OH \cdot CHOH \cdot CH_2OH$ and this structure is proved by the following two facts: (1) When allyl alcohol is carefully oxidized, two hydroxyl groups are added at the position of the double bond; thus,

$$CH_2{:}CH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot CH_2OH$$

(2) By carefully oxidizing glycerol, *glyceric acid* is first formed; thus,

$$CH_2OH \cdot CHOH \cdot CH_2OH \rightarrow CH_2OH \cdot CHOH \cdot COOH;$$

this indicates that glycerol contains one $-CH_2OH$ group. By further oxidation, the glyceric acid is converted into tartronic acid; thus,

$$CH_2OH \cdot CHOH \cdot COOH \rightarrow COOH \cdot CH_2O \cdot COOH;$$

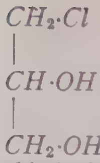
hence, glycerol must contain two $—CH_2OH$ groups, and its composition must be $CH_2OH \cdot CH_2O \cdot CH_2OH$. Now, since tartronic acid still possesses alcoholic properties, the group CH_2O must have the constitution $>CHOH$, and as this group must have the same composition in the glycerol molecule, the structure of glycerol must be as represented by the formula, $CH_2OH \cdot CHOH \cdot CH_2OH$.

111. Properties of Glycerol.—Pure glycerol is a clear, colorless, sirupy liquid, with a sweet, taste, and a specific gravity of 1.260 at 20° C. It is miscible in all proportions with water and alcohol, but is insoluble in ether and chloroform. Cooled below 0° C., it solidifies to a white crystalline mass that melts at 17° C. It boils at 290° C. without decomposition unless salts are present, when it decomposes at this temperature. It can be distilled, entirely unaltered, with superheated steam, but when heated at its boiling point for some time under atmospheric pressure, it decomposes, giving off acrolein, among other products. Glycerol absorbs water from the air, and when heated to 150° C. becomes inflammable and burns with a flame like that of alcohol. It dissolves the alkalies, alkaline earths, and many metallic oxides, forming compounds similar to the alcoholates.

112. Uses.—Glycerol is used in many ways in medicine and in the arts, its chief use being in the manufacture of nitroglycerine. In medicine, it may be used instead of sugar or syrup in sweetening mixtures, or in diabetes. Technically, it is used by brewers and confectioners to sweeten their products. It is also used as a lubricant, for preserving, to keep substances soft and pliant, and in lead-oxide cements. Equal volumes of water and glycerol are used for filling gas meters, as this mixture is much less easily frozen and less liable to dry up than water alone. Mixtures of gelatine and glycerol are also used in the manufacture of duplicating plates and hectographs.

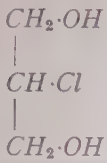
ESTERS OF GLYCEROL

113. Halohydrins.—All of the glycerol esters of the halogen acids are called *halohydrins*. There are two possible isomeric monohalohydrins and dihalohydrins, which are distinguished as α- and β- halohydrins. The trihalohydrins are also known. The following structural formulas show the composition of these isomeric halohydrins:



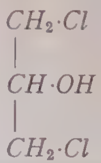
$$\begin{array}{c} CH_2{\cdot}Cl \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}OH \end{array}$$

α-chlorhydrin



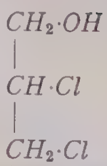
$$\begin{array}{c} CH_2{\cdot}OH \\ | \\ CH{\cdot}Cl \\ | \\ CH_2{\cdot}OH \end{array}$$

β-chlorhydrin



$$\begin{array}{c} CH_2{\cdot}Cl \\ | \\ CH{\cdot}OH \\ | \\ CH_2{\cdot}Cl \end{array}$$

α-dichlorhydrin



$$\begin{array}{c} CH_2{\cdot}OH \\ | \\ CH{\cdot}Cl \\ | \\ CH_2{\cdot}Cl \end{array}$$

β-dichlorhydrin

The *α-halohydrins* are formed when the halogen acids act on glycerol. *β-chlorhydrin* is obtained by the action of hypochlorous acid on allyl alcohol. The *α-dihalohydrins* are produced in the same manner as the corresponding monohalohydrins, while the *β-dihalohydrins* are the result of the addition of halogens to allyl alcohol. The *trihalohydrins* are obtained when halogens are added to the allyl halides, by the action of phosphorus halides on the dihalohydrins, and when iodine chloride acts on propylene chloride.

114. Of the large number of esters formed by glycerol with the fatty acids, only a few of the most important need be mentioned. The formic acid ester is *monoformin*, $C_3H_5(OH)_2{\cdot}COOH$, which is formed when oxalic acid and glycerine are heated together, and when α-monochlorhydrin acts on sodium formate. When monoformin is heated alone it breaks down and *diformin*, $C_3H_5(OH)(COOH)_2$, is produced. Diformin boils at 164° C.

All the acetic acid esters, or *acetins*, are oily liquids that result from the heating together, at various temperatures, of acetic acid and glycerol. *Monacetin*, $C_3H_5(OH)_2{\cdot}(CH_3COO)$, is formed at 100° C. *Diacetin*, $C_3H_5(OH)(CH_3COO)_2$, is formed at 200° C. and boils at 260° C. *Triacetin*, $C_3H_5(CH_3COO)_3$, is formed at 250° C.; the latter ester is present in codliver oil. It boils at 258° C.

115. Nitroglycerine, $C_3H_5(NO_3)_3$.—The most important compound into the manufacture of which glycerol enters, is its nitric-acid ester, glyceryl nitrate, or, as it is more commonly called, *nitroglycerine*. The ester is prepared by treating glycerol with a mixture of concentrated nitric and sulphuric acids, technically known as *mixed acid*. In the process the glycerol is slowly added to the acid as long as it is dissolved.

Then the reaction mixture is poured into water, when the nitroglycerine separates as a heavy, oily liquid. This oil is then washed and dried.

116. Properties.—Nitroglycerine is a heavy, nearly colorless, oily liquid with a specific gravity of 1.6; it volatilizes very energetically at 160° C., and crystallizes at $-20°$ C. It possesses the characteristic sweet taste of glycerol, but is poisonous when taken inwardly, except in very small quantities, when it has a stimulating effect. It is insoluble in water, slightly soluble in alcohol, but dissolves readily in methyl alcohol and ether. When heated rapidly or subjected to shock, it explodes violently. If a piece of paper is moistened with a drop of nitroglycerine and is struck a sharp blow, it will be blown into the smallest fragments. On the application of a flame or red-hot iron, nitroglycerine is comparatively harmless, as it burns very quietly. Heated over a flame in the open air, it explodes but feebly; but if heated in a closed vessel it explodes, at about 150° C. with great violence.

Although large quantities of nitroglycerine in the liquid form are used in the oil fields for opening up wells, its use in this form is ordinarily attended by considerable danger. In order that it may be more convenient for use and more safely handled, it is mixed with infusorial earth. The earth absorbs the nitroglycerine and forms a soft, plastic mass which, in the form of sticks, is known as *dynamite*. A small quantity of guncotton, or nitrocellulose, dissolved in nitroglycerine converts it into an elastic solid called *blasting gelatine*. This is also the base of some smokeless powders.

POLYHYDROXY ALCOHOLS

117. Structure.—Alcohols containing four, five, six, seven, and even more hydroxyl groups are known to exist, and many of them have been studied. The number of hydroxyl groups present in an alcohol is determined by the number of acetyl radicals, CH_3CO, that will enter into the composition of the alcohol on heating it with acetic anhydride and sodium acetate, when the acetyl will replace the hydroxyl. The lowest member of each series of polyhydroxy alcohols must have at least as many carbon atoms as it has hydroxyl radicals. If this were not true, one carbon atom would necessarily be linked to two hydroxyl radicals and the alcohol would be unstable and break up into simpler compounds.

Most of the known higher alcohols are obtained from natural sources. They are distinguished by a sweet taste, and some were, for a considerable time, classed among the sugars, to which they are closely related. The derivatives and oxidation products of these alcohols are similar in constitution to those of glycol.

118. Erythrol, $C_4H_6(OH)_4$.—Erythrol, or erythrite, is the best known of the tetrahydroxy alcohols. It occurs naturally in one of the algae and in some lichens.

Erythrol is prepared from the lichens by boiling them with milk of lime, filtering, removing the excess of lime by means of carbon dioxide, concentrating the filtrate, and treating it with alcohol, when erythrol crystallizes out in white prisms. Erythrol has a slightly sweet taste, is soluble in water, only slightly soluble in alcohol, and insoluble in ether. The crystals melt at 122° C. and boil at 330° C. The structural formula of erythrol is $CH_2OH \cdot CHOH \cdot CHOH \cdot CH_2OH$. Reduction with hydriodic acids converts it into *n*-secondary butyl iodide, $CH_3CHI \cdot CH_2CH_3$.

119. Arabitol, $C_5H_7(OH)_5$ and **Xylitol,** $C_5H_7(OH)_5$.—Arabitol and xylitol, or arabite and xylite, are isomeric compounds. Arabitol is obtained from a sugar, arabinose. It is levorotatory, has a sweet taste, and melts at 102° C.

Xylitol is obtained from a sugar called *xylose*. It is a sirupy liquid possessing a sweet taste, and is optically inactive.

120. Mannitol, $C_6H_8(OH)_6$.—Mannitol, or mannite, a hexahydroxy alcohol, occurs in the vegetable kingdom, being found in olives, celery, rye bread, and in manna, the partly dried sap of the manna ash, which contains from 50 to 60 per cent. of mannitol.

It is obtained from manna by extracting with alcohol and allowing the solution to crystallize. Mannitol is also formed in the fermentation of sugar.

Mannitol crystallizes in two forms, depending on the solvent used. It crystallizes from alcohol in delicate needles, and from water in large, white rhombic prisms. It is quite soluble in water, a little less soluble in alcohol, and insoluble in ether. It has a very sweet taste, and melts at 166° C.

121. Mannitol Hexanitrate, $C_6H_8(O \cdot NO_2)_6$.—Mannitol hexanitrate or nitromannitol is obtained by treating mannitol with fuming nitric acid, or, more easily, by a mixture of nitric and sulphuric acids. This compound crystallizes from alcohol and ether in bright needles, and, like nitroglycerine, is a powerful explosive. When carefully heated, it melts at 108° C. and deflagrates strongly.

122. Dulcitol, $C_6H_8(OH)_6$.—Dulcitol, or dulcite, is a hexahydroxy alcohol that is isomeric with mannitol. It is obtained from Madagascar in a manna, from which it is extracted with boiling water. It may also be prepared by treating either sugar of milk or galactose with nascent hydrogen.

Dulcitol is a viscous substance, crystallizing in large, white, monoclinic prisms, and having a slightly sweet taste. It is less soluble in water than is mannitol, is almost insoluble in alcohol, and melts at 188° C.

123. Sorbitol, $C_6H_8(OH)_6$.—Sorbitol, or sorbite, is another isomeride of mannitol. It occurs in the berries of the mountain ash, in plums and cherries. It forms in minute colorless crystals that are easily soluble in water. It dissolves easily in hot alcohol. When heated, the crystals of sorbitol lose water and melt at 110° C.

ORGANIC CHEMISTRY

(PART 4)

DERIVATIVES OF ALIPHATIC HYDROCARBONS

MONOHYDROXY MONOBASIC ACIDS

COMPOSITION AND PREPARATION

1. Composition.—The monohydroxy monobasic acids are those that contain one hydroxyl group and one carboxyl group in the molecule. Since they contain the hydroxyl group, they have all the properties of the alcohols, and to the carboxyl group they owe their acidic properties. They are sometimes called hydroxy fatty acids because of their origin from the fatty acids by the replacement of hydrogen by the hydroxyl group.

2. Preparation.—The monohydroxy, monobasic acids are prepared by the following general methods:

1. By treating the halogen substitution product of a fatty acid with silver hydroxide or potassium hydroxide; thus,

$$CH_2Cl{\cdot}COOH + AgOH = CH_2OH{\cdot}COOH + AgCl$$

2. By treating the amino derivative of a fatty acid with nitrous acid; thus,

$$CH_2NH_2{\cdot}COOH + HNO_2 = CH_2OH{\cdot}COOH + N_2 + H_2O$$

3. By fusing the sulphonic-acid derivative of a fatty acid with caustic potash; thus,

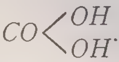
$$CH_2SO_3H{\cdot}COOH + KOH = CH_2OH{\cdot}COOH + KHSO_3$$

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

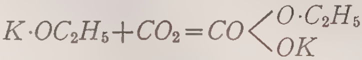
4. By the careful oxidation of poly-hydroxy alcohols; thus,

$$CH_3 \cdot CHOH \cdot CH_2OH + O_2 = CH_3 \cdot CHOH \cdot COOH + H_2O$$

3. Hydroxy Formic Acid, $HO \cdot COOH$.—The first and simplest member of the series, which would be known as hydroxy formic acid, does not exist in the free state, and in fact is nothing but carbonic acid. Owing to its peculiar structure, it is a dibasic acid; the other members of the series are not. It is referred to merely because a few of its derivatives are somewhat closely allied to those of the hydroxy acids proper.

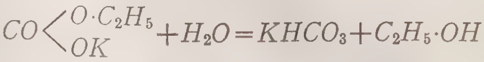


4. Carbonic Acid, $CO{<}\begin{matrix}OH\\OH\end{matrix}$.—Carbonic acid, which may be considered as hydroxy formic acid, $HO \cdot CO \cdot OH$, exists only in the form of its salts. Any attempt to liberate the acid from its salts by means of a stronger acid always causes it to break down. This is another very good example of the instability of compounds in which more than one hydroxyl group is attached to the same carbon atom. Very little is known about this acid except that it is feebly dibasic and readily breaks down into water and carbon dioxide. The ethereal salts of carbonic acid are made by treating the alcoholic solution of an alkali alcoholate with carbon dioxide, CO_2, forming the *primary esters*; this is shown by the equation



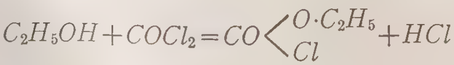
$$K \cdot OC_2H_5 + CO_2 = CO{<}\begin{matrix}O \cdot C_2H_5\\OK\end{matrix}$$

These primary esters are very unstable in a free condition, water decomposing them into the alkali carbonate and alcohol; for example,

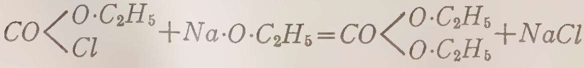


$$CO{<}\begin{matrix}O \cdot C_2H_5\\OK\end{matrix} + H_2O = KHCO_3 + C_2H_5 \cdot OH$$

The neutral esters are made by treating the alcohols with carbonyl chloride and sodium alcoholate as is shown by the equations

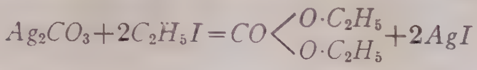


$$C_2H_5OH + COCl_2 = CO{<}\begin{matrix}O \cdot C_2H_5\\Cl\end{matrix} + HCl$$



$$CO{<}\begin{matrix}O \cdot C_2H_5\\Cl\end{matrix} + Na \cdot O \cdot C_2H_5 = CO{<}\begin{matrix}O \cdot C_2H_5\\O \cdot C_2H_5\end{matrix} + NaCl$$

and by the action of alkyl iodides on silver carbonate; thus,

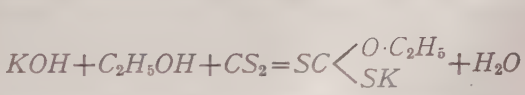


$$Ag_2CO_3+2C_2H_5I=CO<\begin{matrix}O\cdot C_2H_5\\O\cdot C_2H_5\end{matrix}+2AgI$$

The neutral esters are all liquids, are soluble in water, and have an ethereal odor. With the exception of the dimethyl and the methyl ethyl ester all are lighter than water.

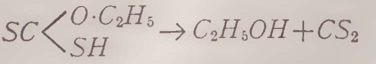
5. Ethyl Chlorcarbonate, $CO<\begin{matrix}O\cdot C_2H_5\\Cl\end{matrix}$.—Ethyl chlorcarbonate is prepared by treating alcohol with carbonyl chloride. This compound may be considered as the ethyl ester of monochlorformic acid, and hence should be called *ethyl chlorformate*. It is a colorless liquid with a pungent taste and a suffocating odor. Its specific gravity is 1.44, it boils at 94° C., and is soluble in water and alcohol.

As carbon disulphide acts very similarly to carbon dioxide toward the alkalies and alcohols, many ethereal salts containing sulphur can be prepared. Thus, *potassium xanthogenate*, $SC<\begin{matrix}O\cdot C_2H_5\\SK\end{matrix}$, is formed by treating an alcoholic solution of caustic potash with carbon disulphide. This is shown by the equation



$$KOH+C_2H_5OH+CS_2=SC<\begin{matrix}O\cdot C_2H_5\\SK\end{matrix}+H_2O$$

Free xanthogenic acid resembles carbonic acid in that it is very unstable and breaks up into alcohol and carbon disulphide; thus,

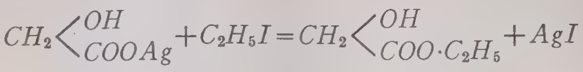


$$SC<\begin{matrix}O\cdot C_2H_5\\SH\end{matrix}\rightarrow C_2H_5OH+CS_2$$

6. Hydroxy Acetic Acid, $CH_2<\begin{matrix}OH\\COOH\end{matrix}$.—Hydroxy acetic acid, or glycolic acid, is found in nature in the leaves of the wild grape and in unripe grapes. It is usually prepared by treating monochloracetic acid with caustic potash; thus,

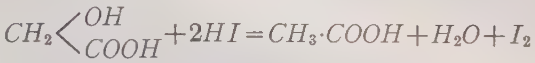
$$CH_2Cl\cdot COOH+KOH=CH_2\cdot OH\cdot COOH+KCl$$

Glycolic acid is a colorless, crystalline solid that is soluble in water, alcohol, and ether, and melts at 80° C. Glycolic acid forms a series of salts with metals and ethereal salts with alcohol radicals. Ethyl glycolate, an example of the latter, is made in the usual way, by treating silver glycolate with ethyl iodide; thus,



$$CH_2 < \begin{array}{l} OH \\ COOAg \end{array} + C_2H_5I = CH_2 < \begin{array}{l} OH \\ COO \cdot C_2H_5 \end{array} + AgI$$

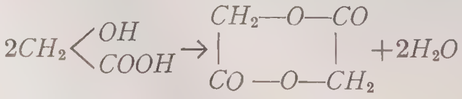
Glycolic acid forms acid ethers when the hydrogen of its hydroxyl group is replaced by an alkyl radical. One of these ethers is *ethyl glycolic acid*, $CH_2 < \begin{array}{l} O \cdot C_2H_5 \\ COOH \end{array}$, which is isomeric ethyl glycolate, but differs from the latter in that it has acid properties. In the formation of ethyl glycolate, the alcoholic hydroxyl remains unchanged; this fact is true of all the salts of glycolic acid. Reducing agents convert glycolic acid into acetic acid, as is shown by the equation



$$CH_2 < \begin{array}{l} OH \\ COOH \end{array} + 2HI = CH_3 \cdot COOH + H_2O + I_2$$

The metallic glycolates are all more or less soluble in water and are all crystallizable.

When glycolic acid is heated, or when it is distilled *in vacuo*, it loses water and yields the anhydride glycolide. The reaction is shown by the following equation:



$$2CH_2 < \begin{array}{l} OH \\ COOH \end{array} \rightarrow \begin{array}{|lcr|} CH_2 - O - CO & & \\ & & \\ CO - O - CH_2 & & \end{array} + 2H_2O$$

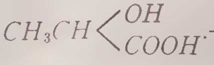
Glycolide is insoluble in cold water, but on long-continued boiling with water it is finally converted into glycolic acid.

HYDROXY PROPIONIC ACIDS

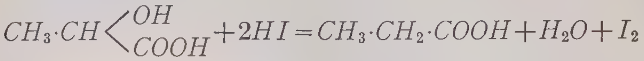
7. Isomerism.—When the structure of propionic acid was discussed, it was shown that two isomeric derivatives were possible by the replacement of hydrogen atoms attached to different carbon atoms. Hence, by the replacement of these hydrogen atoms by hydroxyl, isomeric hydroxy propionic acids are obtained. One of these is called α-hydroxy propionic acid or lactic acid, and the other, β-hydroxy propionic acid or hydracrylic acid.

8. Stereoisomerism.—As previously stated, stereoisomeric compounds have the same formulas, and conduct themselves chemically in a similar manner, but differ in their physical properties, as in their action toward polarized light. In order to have this property, or to be optically active, a body must contain one or more carbon atoms to each of which are attached four different radicals or elements. This carbon atom is said to be asymmetric, and the property of being levorotatory or dextrorotatory depends on the arrangement in space of the four different radicals or atoms grouped about this asymmetric carbon atom. The hydroxy propionic acids furnish a very good illustration of stereoisomerism.

In addition to the two isomeric hydroxy propionic acids, there are two other acids of exactly the same composition. These acids have also been shown to have the structure of *α*-hydroxy propionic acid. Therefore, there are three known *α*-hydroxy propionic acids having the same structure but differing from each other in their physical properties. These acids have names which depend upon the manner in which they rotate the plane of polarized light. They are *inactive lactic acid*, or ordinary lactic acid; *dextrolactic acid*, or *sarcolactic acid*, and *levolactic acid*.

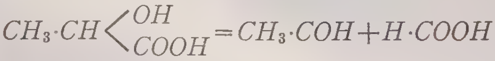
9. Inactive Lactic Acid,  $CH_3CH{<}\begin{matrix}OH\\COOH\end{matrix}$.—As the name indicates, inactive lactic acid does not rotate the plane of polarized light. It is sometimes called *inactive ethylidene lactic acid* or lactic acid of fermentation, and occurs in many substances that have soured, such as sour milk, sour kraut, pickles, and the gastric juice. It is prepared by the action of the lactic-acid bacillus on various sugars such as milk sugar, cane sugar, gum, and starch. The process is best carried out by dissolving cane sugar in water, and after adding sour milk and cheese, allowing the whole to stand at a temperature of 30° to 35° C. As the fermentation is impossible in a lactic-acid solution of more than a certain concentration, zinc carbonate is added to neutralize the acid. The zinc lactate formed is decomposed, by means of hydrogen sulphide, lactic acid being set free.

Lactic acid can also be prepared by heating dextrose or invert sugar with caustic soda. It is a colorless, sirupy, odorless acid, with a specific gravity of 1.206 at 25° C. It readily absorbs moisture from damp air and is miscible with ether and all proportions of water and alcohol. Heated to 130° C., it is slowly converted into the anhydride, and hydriodic acid reduces it to propionic acid; thus,

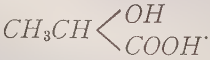


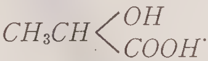
$$CH_3\cdot CH\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.+2HI=CH_3\cdot CH_2\cdot COOH+H_2O+I_2$$

Continued heating alone or with sulphuric acid causes it to break down into acetaldehyde and formic acid; thus,



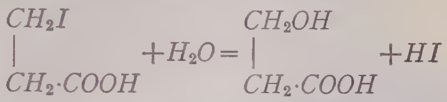
$$CH_3\cdot CH\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.=CH_3\cdot COH+H\cdot COOH$$

10. Dextrolactic Acid,  $CH_3CH\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$.—Dextrolactic acid, or sarcolactic acid, is found in muscular tissue and in the liquids extracted from meat, and while it must be represented by the same structural formula, it is different from inactive lactic acid. Its properties and its behavior toward reagents are, in all respects, like those of inactive lactic acid, although its salts are somewhat more soluble. The chief difference lies in its action toward polarized light. The dextro acid turns the plane of polarization to the right and its salts are levorotatory; the inactive acid and its salts exert no action whatever on polarized light.

11. Levolactic Acid,  $CH_3CH\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$.—Levolactic acid, the third modification of lactic acid, rotates the plane of polarized light to the left. Its salts, however, are dextrorotatory. It is formed by the fractional crystallization of the strychnine salt of ordinary inactive lactic acid, when both the dextrolactic and levolactic acids are obtained.

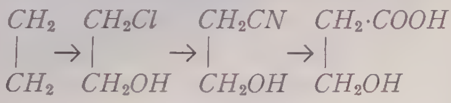
12. Hydracrylic Acid, $CH_2OH\cdot CH_2COOH$.—Hydracrylic acid owes its name to the fact that it is formed when acrylic acid takes up one molecule of water. The reaction takes place when acrylic acid is heated with sodium hydroxide to 100° C.

In a similar manner, when hydracrylic acid is heated, acrylic acid is formed. Hydracrylic acid is also known as β-hydroxy propionic acid and as ethylene lactic acid. It is isomeric with ethylidene lactic acid and is prepared by treating β-iodopropionic acid, or β-chlorpropionic acid with moist silver oxide. This reaction is shown by the equation



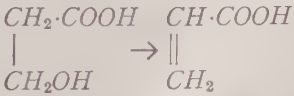
$$\begin{array}{l}CH_2I\\ |\\ CH_2{\cdot}COOH\end{array} + H_2O = \begin{array}{l}CH_2OH\\ |\\ CH_2{\cdot}COOH\end{array} + HI$$

The structure of hydracrylic acid is clearly shown by its synthesis. Ethylene is treated with hypochlorous acid, which converts it into ethylene chlorhydrin. The chlorine is replaced by cyanogen, and the cyanhydrin is converted into hydracrylic acid by boiling with an alkali; thus,



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array} \rightarrow \begin{array}{l}CH_2Cl\\ |\\ CH_2OH\end{array} \rightarrow \begin{array}{l}CH_2CN\\ |\\ CH_2OH\end{array} \rightarrow \begin{array}{l}CH_2{\cdot}COOH\\ |\\ CH_2OH\end{array}$$

The free acid is a thick, sirupy liquid and does not crystallize. On heating, it loses water and forms acrylic acid as follows:



$$\begin{array}{l}CH_2{\cdot}COOH\\ |\\ CH_2OH\end{array} \rightarrow \begin{array}{l}CH{\cdot}COOH\\ \|\\ CH_2\end{array}$$

A very interesting difference in conduct between ethylidene lactic acid and ethylene lactic acid is noted when they are heated. When the former is heated, its acid and alcoholic properties are both destroyed; when the latter is heated only the alcoholic properties are destroyed.

13. Lactic acid forms salts known as *lactates*, the best defined of which are represented by the formulas $\left(CH_3{-}CH{<}\begin{smallmatrix}OH\\ COO\end{smallmatrix}\right)M'$ and $\left(CH_3{-}CH{<}\begin{smallmatrix}OH\\ COO\end{smallmatrix}\right)_2M''$. They are sparingly soluble in water, insoluble in ether, and their crystals effloresce rapidly. *Sodium lactate*, $CH_3{-}CH{<}\begin{smallmatrix}OH\\ COONa\end{smallmatrix}$, is obtained as a thick, sirupy liquid when lactic acid is neutralized with sodium carbonate. On heating with metallic sodium, *disodium lactate*, $CH_3—CH\left\langle\begin{smallmatrix}ONa,\\ COONa\end{smallmatrix}\right.$, is obtained. *Calcium lactate*, $\left(CH_3—CH\left\langle\begin{smallmatrix}OH\\ COO\end{smallmatrix}\right.\right)_2Ca$, is formed in the preparation of lactic acid. It crystallizes with five molecules of water.

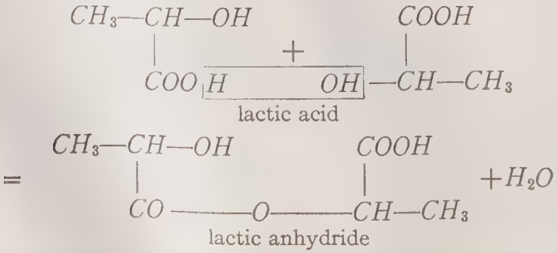
EFFECTS OF HEAT ON MONOHYDROXY MONOBASIC ACIDS

14. Names and Illustrations.—The monohydroxy monobasic acids are designated α, β, γ, and δ, depending on the position of the hydroxyl group with reference to the carboxyl group. The acids in which the hydroxyl radical is united to the same carbon atom as the carboxyl radical, are known as a *α-hydroxy acids*. If the hydroxyl radical is united with the next carbon atom, the acid is known as a *β-hydroxy acid*. Examples, however, will tend to make this clearer, thus; α-hydroxy acids have the formulas

$$CH_2\left\langle\begin{smallmatrix}OH\\ COOH\end{smallmatrix}\right., \quad CH_3{\cdot}CH\left\langle\begin{smallmatrix}OH\\ COOH\end{smallmatrix}\right., \text{ and } CH_3{\cdot}CH_2{\cdot}CH\left\langle\begin{smallmatrix}OH\\ COOH\end{smallmatrix}\right..$$

β-hydroxy acids have the formulas $\begin{array}{l}CH_2(OH)\\ \vert\\ CH_2{\cdot}COOH\end{array}$ and $\begin{array}{l}CH_3{\cdot}CH(OH)\\ \vert\\ CH_2{\cdot}COOH\end{array}$. *γ-hydroxy acids* are $CH_2OH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, and *δ-hydroxy acids* have the formula $CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

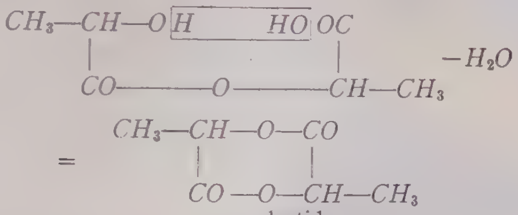
15. Lactides.—On heating an α-hydroxy acid, two molecules of it react, one with the other, water being eliminated and an anhydride formed.



lactic acid

lactic anhydride

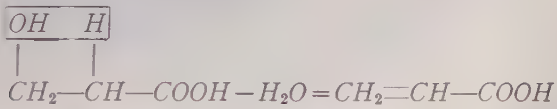
Thus, it is seen that the hydroxyl group of one molecule reacts with the hydrogen of the carboxyl group of the other molecule, to form the anhydride. Upon continued heating, the anhydride also loses a molecule of water, a lactide being formed.



$$\begin{array}{lll} CH_3-CH-O\boxed{H \qquad HO}OC & & \\ \qquad\;\; | \qquad\qquad\qquad\;\; | & & -H_2O \\ \qquad\;\; CO-\!\!-\!\!-O-\!\!-\!\!-CH-CH_3 & & \\ & & \\ \qquad\qquad CH_3-CH-O-CO & & \\ = \qquad\qquad\quad | \qquad\quad | & & \\ \qquad\qquad\qquad CO-O-CH-CH_3 & & \end{array}$$

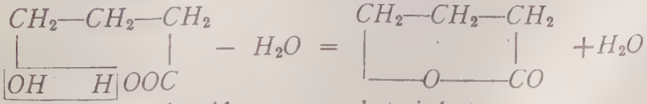
lactide

16. Beta-Hydroxy Acid Anhydrides.—On heating β-hydroxy acids, water is eliminated from one molecule only, an unsaturated acid being formed. The formation of acrylic acid serves as an illustration:



$$\begin{array}{l} \boxed{OH \quad H} \\ \;\;| \qquad\; | \\ CH_2-CH-COOH-H_2O=CH_2=CH-COOH \end{array}$$

17. Lactones.—The γ- and δ- hydroxy acids are distinguished from the α- and β-acids by the fact that they lose water very readily, forming lactones. Some of the γ-acids have this tendency to such a degree that when they are liberated from their salts, they at once give up one molecule of water, forming the corresponding lactone. For this reason many of the γ-acids are known only in the form of their esters or salts. Thus, in many cases, when a solution of the acid is treated with a mineral acid the acid corresponding to the salt is not precipitated but a lactone is formed instead. This change is shown by the following equation:



$$\begin{array}{lcl} CH_2-CH_2-CH_2 & & CH_2-CH_2-CH_2 \\ |\qquad\qquad\qquad\;\; | \quad -H_2O & = & |\qquad\qquad\qquad\;\; | \quad +H_2O \\ \boxed{OH \quad H}OOC & & \;-\!\!-O-\!\!-CO \end{array}$$

hydroxy butyric acid butyric lactone

The lactones of the δ-hydroxy acids do not have the stability of the γ-lactones but gradually absorb water at the ordinary temperature, regenerating the acids.

SATURATED DIBASIC ACIDS

18. General Properties.—The dibasic acids may be regarded as being derived from the paraffins by the replacement of two atoms of hydrogen by two carboxyl groups. The acids of this series are all well-defined crystalline substances. Many of them are soluble in water, and all have strong acid reactions, forming an acid and a neutral series of salts. They are characterized by their behavior when heated, depending on the position of the carboxyl groups. Those that have the carboxyl groups attached to the same carbon atom break down into a monobasic acid and carbon dioxide; those having the carboxyl groups attached to different carbon atoms do not give off carbon dioxide, but lose water and form anhydrides.

TABLE I

PHYSICAL PROPERTIES OF DIBASIC ACIDS

Name of Acid	Formula	Melting Point Degrees C.
Oxalic	$CO_2H\cdot CO_2H$	187.0* 101†
Malonic	$CH_2(CO_2H)_2$	132.0
Succinic	$C_2H_4(CO_2H)_2$	185.0
Pyrotartaric	$C_3H_6(CO_2H)_2$	98.0
Adipic	$C_4H_8(CO_2H)_2$	153.0
Pimelic	$C_5H_{10}(CO_2H)_2$	105.5
Suberic	$C_6H_{12}(CO_2H)_2$	141.0
Azelaic	$C_7H_{14}(CO_2H)_2$	108.0
Sebacic	$C_8H_{16}(CO_2H)_2$	134.5
Brassylic	$C_9H_{18}(CO_2H)_2$	110.0

*Anhydrous. †Hydrated.

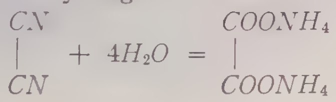
The melting points of these acids have the peculiarity that the members with an even number of carbon atoms have higher melting points than those immediately succeeding them, with an uneven number of carbon atoms, as is shown in Table I. These melting points, however, approach more and more closely as the number of the carbon atoms increases.

Another peculiarity of the dibasic acids is their solubility in water. Those with an uneven number of carbon atoms are far more soluble in water than those containing an even number of carbon atoms, but this solubility diminishes with the increase in the number of carbon atoms.

Many of the dibasic acids are prepared by special methods. The general methods used for their preparation are analogous to those used in the preparation of the monobasic acids. Thus they may be prepared by the oxidation of the corresponding glycols and aldehydes and by the hydrolysis of dinitriles.

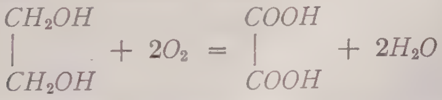
19. Oxalic Acid, $(COOH)_2$.—Oxalic acid, the first and most important member of the series, is prepared by a variety of methods. Therefore, only those of the greatest theoretical importance and those of the most practical value will be considered.

1. Hydrolysis of cyanogen:



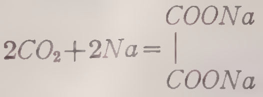
$$\begin{array}{l}CN\\|\\CN\end{array} + 4H_2O = \begin{array}{l}COONH_4\\|\\COONH_4\end{array}$$

2. Oxidation of ethylene glycol:



$$\begin{array}{l}CH_2OH\\|\\CH_2OH\end{array} + 2O_2 = \begin{array}{l}COOH\\|\\COOH\end{array} + 2H_2O$$

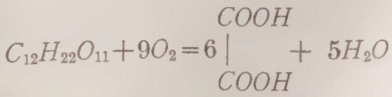
3. By passing carbon dioxide over sodium heated to 360° C.; thus,



$$2CO_2+2Na=\begin{array}{l}COONa\\|\\COONa\end{array}$$

20. Commercial Manufacture.—Oxalic acid is manufactured on a large scale by the following methods.

1. By the oxidation of sugar with nitric acid according to the reaction:



$$C_{12}H_{22}O_{11}+9O_2=6\begin{array}{l}COOH\\|\\COOH\end{array} + 5H_2O$$

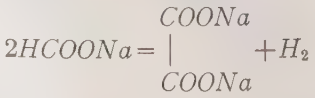
Sugar is heated gently in a retort with five times its weight of strong nitric acid, the heat being removed when the action begins and copious red fumes are evolved. When the action ceases, heat is again applied to the retort and the liquid concentrated by driving off the excess of nitric acid until it deposits crystals on cooling. These are drained, dissolved in water, and recrystallized.

2. By heating a mixture of caustic potash and caustic soda to the point of fusion with sawdust. Ordinary pine sawdust is heated with a mixture of $KOH+2NaOH$, having a specific gravity of 1.35, for some hours at a temperature of from 200° C. to 220° C., without allowing the mass to become charred. A formate is an intermediate product which on further heating loses hydrogen, the final product being a gray powder of sodium oxalate. This product is now treated with water at 15.5° C., which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off and the alkalies causticized and used again. The sodium oxalate is washed, decomposed with slaked lime, and the resulting calcium oxalate decomposed with sulphuric acid. The liquid decanted from the calcium sulphate is crystallized in lead vessels, and the crystals of oxalic acid further purified by recrystallization.

3. Probably the latest method to be used in the large-scale production of oxalic acid is that on which the Goldschmidt process is based. According to this method carbon monoxide is passed over a heated mixture of sodium hydroxide and coke, sodium formate being formed. Thus,

$$NaOH+CO=HCOONa$$

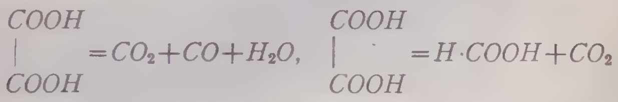
When sodium formate is heated to about 400° C., two molecules unite to form sodium oxalate.



$$2HCOONa=\begin{array}{l}COONa\\ |\\ COONa\end{array}+H_2$$

The oxalic acid is then prepared from the sodium salt as already described.

21. Properties.—Oxalic acid crystallizes from an aqueous solution in colorless, transparent, monoclinic prisms with two molecules of water, which effloresce at 20° C. in dry air and which are lost at 105° C. It has a very acid taste, melts at 101° C., and is soluble in water and alcohol but only lightly soluble in ether. The anhydrous oxalic acid melts at 187° C. Large quantities taken into the system are poisonous, having a retarding action on the heart and depressing the functions of the nerve centers. Its antidote is chalk or precipitated calcium carbonate. Heated carefully to 150° C., the anhydrous acid sublimes without undergoing decomposition. When heated strongly, it decomposes with the formation of carbon dioxide, carbon monoxide, and water. When heated with sulphuric acid, formic acid and carbon dioxide are the products formed; thus,



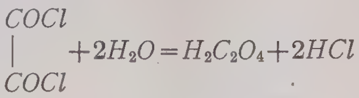
$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} = CO_2 + CO + H_2O, \quad \begin{matrix} COOH \\ | \\ COOH \end{matrix} = H \cdot COOH + CO_2$$

Oxalic acid is readily oxidized. The equation representing the reaction which takes place when it is oxidized by potassium permanganate is written as follows:

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

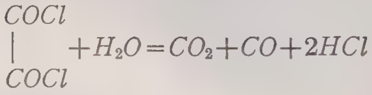
A solution of oxalic acid, or better, a solution of ammonium oxalate added to a solution of calcium chloride, forms a white precipitate of calcium oxalate, even in very dilute solutions, that is insoluble in acetic acid or ammonium hydroxide.

22. Oxalic acid forms esters with organic compounds, both the acid and the neutral esters being formed simultaneously when anhydrous oxalic acid is heated with alcohols. They are separated by distillation under reduced pressure. *Dimethyl* at *oxalate*, $C_2O_4(CH_3)_2$, is a solid that melts at 54° C. and distils 163° C.; it is formed in the preparation of pure methyl alcohol, *Diethyl oxalate*, $C_2O_4(C_2H_5)_2$, is a liquid that boils at 186° C. *Oxalyl chloride*, $\begin{matrix} COCl \\ | \\ COCl \end{matrix}$, is formed when two parts of phosphorus pentachloride and one part of oxalic acid react. It is a colorless liquid that boils at 64° C. and solidifies to a white crystalline mass at $-12°$ C. Its vapor, when brought into contact with water in the form of steam, is converted into oxalic and hydrochloric acids; thus,



$$\begin{array}{l} COCl \\ | \\ COCl \end{array} + 2H_2O = H_2C_2O_4 + 2HCl$$

Water, on the other hand, converts it into CO_2, CO, and HCl; thus,

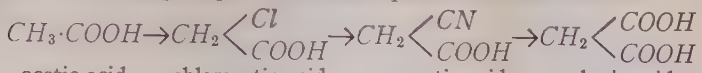


$$\begin{array}{l} COCl \\ | \\ COCl \end{array} + H_2O = CO_2 + CO + 2HCl$$

23. Oxalic acid forms an acid salt and a neutral salt with the metals. All the salts, except those of the alkali metals are insoluble. *Ammonium oxalate*, $(NH_4)_2C_2O_4+2H_2O$, occurs in Peruvian guano and also in some urinary calculi. Its principal use is in analysis for the determination of calcium. *Calcium oxalate*, $CaC_2O_4+4H_2O$, occurs crystallized in plant cells and some plants growing in soils rich in limestone sometimes contain as much as half their entire weight of calcium oxalate. *Acid potassium oxalate*, $KHC_2O_4+2H_2O$, is found in the sorrels or plants of the oxalis variety. It is frequently misnamed *essential salt of lemons*. *Potassium ferrous oxalate*, $K_2Fe(C_2O_4)_2$, yields a yellow solution, is a strong reducing agent, and is frequently used as a developer for photographic plates. *Potassium ferric oxalate*, $K_3Fe(C_2O_4)_3$, yields a green solution, which is rapidly reduced in sunlight. This property is made use of in the preparation of blueprint and platinotype photographic papers. *Manganese oxalate*, $Mn(C_2O_4)+2H_2O$, is used as a drier in the manufacture of varnishes.

Oxalic acid is used largely in calico printing, in dyeing and bleaching, cleaning brass, in removing iron stains from linen, and in the manufacture of blueprint and platinum photographic papers.

24. Malonic Acid, $CH_2(COOH)_2$.—Malonic acid, the second member of the series, may be prepared from the cyanide derivative of a monobasic acid, usually acetic acid, according to the following steps, which also prove its constitution:



$$CH_3\cdot COOH \rightarrow CH_2\left\langle\begin{matrix}Cl\\ COOH\end{matrix}\right. \rightarrow CH_2\left\langle\begin{matrix}CN\\ COOH\end{matrix}\right. \rightarrow CH_2\left\langle\begin{matrix}COOH\\ COOH\end{matrix}\right.$$

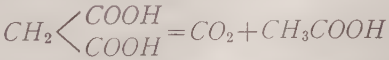
acetic acid chloracetic acid cyanacetic acid malonic acid

The cyanacetic acid is boiled with an alkali, forming the alkali malonate. The excess of the alkali is neutralized with hydrochloric acid and the malonic acid is precipitated as calcium malonate. This, in turn, is boiled with oxalic acid, when the calcium oxalate is precipitated and the malonic acid is crystallized from the solution.

Malonic acid can also be prepared by the hydrolysis of a dicyanide such as dicyano methane, $CH_2(CN)_2$, which is formed by the action of potassium cyanide on dichlor methane.

$$CH_2Cl_2+2KCN=2KCl+CH_2(CN)_2$$
$$CH_2(CN)_2+4H_2O=CH_2(COOH)_2+2NH_3$$

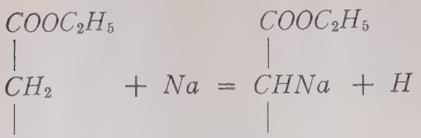
25. Properties.—Malonic acid is a white crystalline solid, crystallizing in triclinic prisms that melt at 132° C. and are easily soluble in water, alcohol, and ether. If heated above its melting point, carbon dioxide is given off and acetic acid is formed. This is shown by the equation



$$CH_2\left\langle\begin{matrix}COOH\\ COOH\end{matrix}\right. = CO_2+CH_3COOH$$

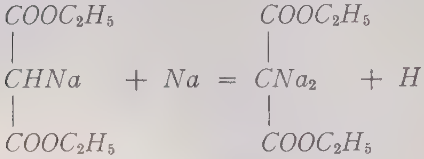
The homologs of malonic acid act in the same manner; in fact, it has been found that when a compound with two carboxyl groups in combination with one carbon atom is heated above its melting point, its molecule loses one molecule of carbon dioxide.

26. Malonic-Ester Synthesis.—Like oxalic acid, malonic acid forms two classes of salts and esters. The ethyl ester, *diethyl malonate*, $CH_2(COOC_2H_5)_2$, is the most important derivative of malonic acid, because of the many important syntheses accomplished with its aid. It is a liquid with a specific gravity of 1.061; it boils at 198° C. and has a faint odor. On treatment with sodium either a *diethyl monosodiomalonate* or a *diethyl disodiomalonate* is formed.



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH_2 \\ | \\ COOC_2H_5 \end{array} + Na = \begin{array}{l} COOC_2H_5 \\ | \\ CHNa \\ | \\ COOC_2H_5 \end{array} + H$$

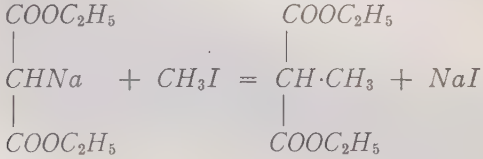
diethyl monosodiomalonate



$$\begin{array}{l} COOC_2H_5 \\ | \\ CHNa \\ | \\ COOC_2H_5 \end{array} + Na = \begin{array}{l} COOC_2H_5 \\ | \\ CNa_2 \\ | \\ COOC_2H_5 \end{array} + H$$

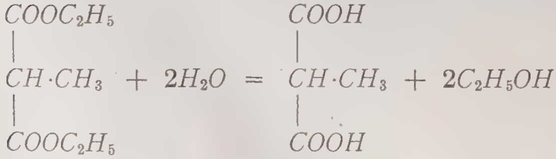
diethyl disodiomalonate

When these compounds are treated with an alkyl iodide, an ester is obtained, which, upon hydrolysis, yields a homolog of malonic acid.



$$\begin{array}{l} COOC_2H_5 \\ | \\ CHNa \\ | \\ COOC_2H_5 \end{array} + CH_3I = \begin{array}{l} COOC_2H_5 \\ | \\ CH{\cdot}CH_3 \\ | \\ COOC_2H_5 \end{array} + NaI$$

diethyl ester of
methyl malonic acid



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH{\cdot}CH_3 \\ | \\ COOC_2H_5 \end{array} + 2H_2O = \begin{array}{l} COOH \\ | \\ CH{\cdot}CH_3 \\ | \\ COOH \end{array} + 2C_2H_5OH$$

methyl malonic acid

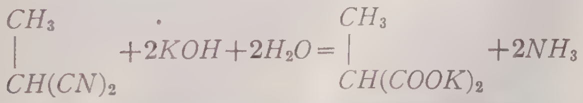
27. It is also possible to introduce two different alkyl groups into diethyl malonate. Thus, when diethyl monosodiomalonate is treated with methyl iodide, the diethyl ester of methylmalonic acid is formed, and on treatment with sodium this again yields a sodio compound, which is converted by ethyl iodide into the diethyl ester of methyl-ethyl malonic acid.

From this it is evident that it is possible to synthesize a great number of dibasic acids from diethyl malonate, and as all these acids have two carboxyl groups united to one carbon atom, and have in common with malonic acid the property of losing carbon dioxide when heated above their melting points, it is evident that the so-called malonic ester synthesis is also available for the preparation of the monobasic fatty acids. As an example of this, methyl ethyl malonic acid loses carbon dioxide on heating, yielding methyl ethyl acetic acid, which is identical in constitution with active valeric acid, which is monobasic.

When monobasic acids of the aliphatic series are heated with an alkali such as sodium hydroxide or calcium hydroxide, they lose carbon dioxide, the corresponding hydrocarbon being formed. Thus the malonic ester synthesis provides a means of preparing the dibasic acids, monobasic acids, and hydrocarbons of the aliphatic series.

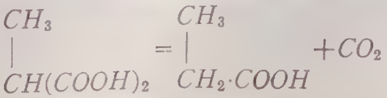
The true anhydride of malonic acid, $CH_2 \genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup} O$, analogous to the anhydrides of the higher members of this series, is unknown.

28. Methyl Malonic Acid, $CH \cdot CH_3(COOH)_2$.—The preparation of methyl malonic acid from diethyl monosodiomalonate has been given. Another method for the preparation of this acid, and one that proves its constitution, is carried out by treating ethylidene cyanide with potassium hydroxide; thus,



$$\begin{array}{l} CH_3 \\ | \\ CH(CN)_2 \end{array} + 2KOH + 2H_2O = \begin{array}{l} CH_3 \\ | \\ CH(COOK)_2 \end{array} + 2NH_3$$

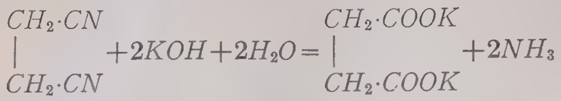
Methyl malonic acid is a white crystalline solid, crystallizing in needles that melt at 130° C. Heated to 150° C., it breaks up into propionic acid and carbon dioxide; thus,



$$\begin{array}{l} CH_3 \\ | \\ CH(COOH)_2 \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2 \cdot COOH \end{array} + CO_2$$

29. Succinic Acid, $C_2H_4(COOH)_2$.—Succinic acid, which is also known as *dicarboxyethane*, may be regarded as being derived from ethane by the replacement of two hydrogen atoms with two carboxyl groups. It derives its name from the Latin *succinum* (amber), one of its natural sources. It is also found in resins, lignite, unripe fruits, and in animal fluids.

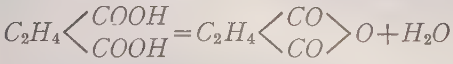
It is synthetically prepared in a number of ways, the structure being shown by the reaction that takes place when ethylene cyanide is treated with a caustic alkali



$$\begin{array}{l}CH_2\cdot CN\\ |\\ CH_2\cdot CN\end{array}+2KOH+2H_2O=\begin{array}{l}CH_2\cdot COOK\\ |\\ CH_2\cdot COOK\end{array}+2NH_3$$

The acid is obtained from the salt by the usual methods, but commercially it is obtained by the distillation of amber.

30. Properties and Salts.—Succinic acid is a colorless solid, crystallizing in monoclinic prisms. It is odorless, has an acrid taste, and melts at 182° C. It is soluble in water and alcohol, but is only slightly soluble in ether. It boils at 235° C., giving up water and forming the anhydride according to the equation.

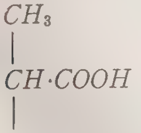


$$C_2H_4<\begin{array}{l}COOH\\ COOH\end{array}=C_2H_4<\begin{array}{l}CO\\ CO\end{array}>O+H_2O$$

The most interesting salt of succinic acid is the *basic ferric succinate*, $Fe_2(C_4H_4O_4)_2(OH)_2$, which is a reddish-brown substance insoluble in water, and can, therefore, be used in analytic work in separating iron and aluminum from manganese, zinc, nickel, and cobalt. A neutral solution of ammonium succinate will always form this salt, when added to a solution containing a ferric salt.

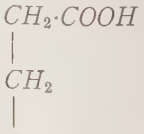
The preparation of *isosuccinic acid* or methyl malonic acid has been given.

31. Pyrotartaric Acid, $(CH_2)_3\cdot(COOH)_2$.—Pyrotartaric acid is known in four isomeric modifications, but only one of these, glutaric acid, is of sufficient importance to warrant description. The various acids with this formula are:



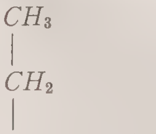
$$\begin{array}{l}CH_3\\ |\\ CH\cdot COOH\\ |\\ CH_2\cdot COOH\end{array}$$

pyrotartaric acid



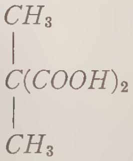
$$\begin{array}{l}CH_2\cdot COOH\\ |\\ CH_2\\ |\\ CH_2\cdot COOH\end{array}$$

glutaric acid



$$\begin{array}{l}CH_3\\ |\\ CH_2\\ |\\ CH(COOH)_2\end{array}$$

ethylmalonic acid

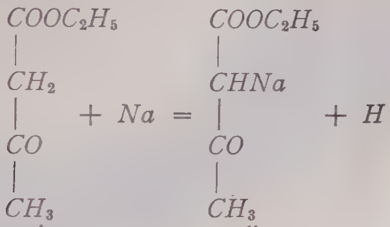


$$\begin{array}{l}CH_3\\ |\\ C(COOH)_2\\ |\\ CH_3\end{array}$$

dimethyl malonic acid

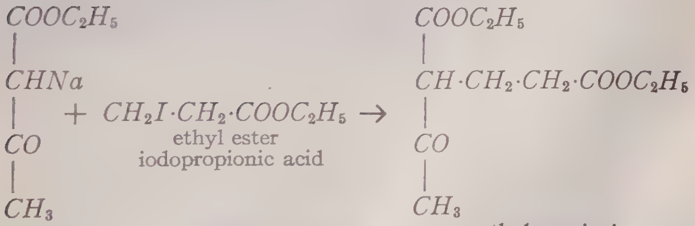
32. Methods of Preparation.—The synthetic preparation of glutaric acid is interesting from a theoretical standpoint in that it illustrates the uses to which aceto acetic ester and malonic acid ester can be put in building up organic compounds.

In one method for the synthesis of glutaric acid, aceto acetic ester, is treated with metallic sodium forming monosodium aceto acetic ester, which, when treated with the ethyl ester of iodo propionic acid, forms ethyl propionic aceto acetic ester. These reactions are illustrated by the following equations:



$$\begin{array}{l}COOC_2H_5\\ |\\ CH_2\\ |\\ CO\\ |\\ CH_3\end{array} + Na = \begin{array}{l}COOC_2H_5\\ |\\ CHNa\\ |\\ CO\\ |\\ CH_3\end{array} + H$$

aceto acetic ester
monosodium
aceto acetic ester

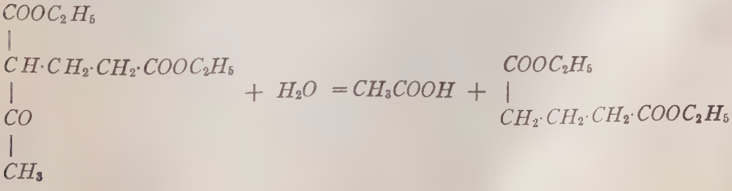


$$\begin{array}{l}COOC_2H_5\\ |\\ CHNa\\ |\\ CO\\ |\\ CH_3\end{array} + CH_2I{\cdot}CH_2{\cdot}COOC_2H_5 \rightarrow \begin{array}{l}COOC_2H_5\\ |\\ CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5\\ |\\ CO\\ |\\ CH_3\end{array}$$

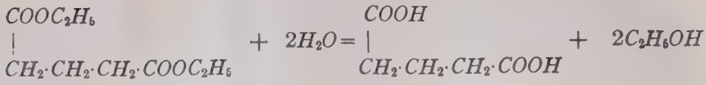
ethyl ester
iodopropionic acid

ethyl propionic
aceto acetic ester

When the ethyl propionic aceto acetic ester is hydrolyzed by means of a concentrated caustic solution, acetic acid, and the diethyl ester of glutaric acid are obtained. Further hydrolysis of the latter gives the acid. The following equations represent the reactions that take place:



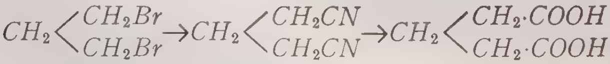
$$\begin{array}{l}COOC_2H_5\\ |\\ CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5\\ |\\ CO\\ |\\ CH_3\end{array} + H_2O = CH_3COOH + \begin{array}{l}COOC_2H_5\\ |\\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5\end{array}$$



$$\begin{array}{l} COOC_2H_5 \\ | \\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5 \end{array} + 2H_2O = \begin{array}{l} COOH \\ | \\ CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \end{array} + 2C_2H_5OH$$

In another method, two molecules of diethyl monosodiomalonate react with methylene iodide, CH_2I_2, to form a product, which, on losing carbon dioxide, forms glutaric acid.

By a third method, and the one that best shows its structure, glutaric acid is prepared from trimethylene bromide by treatment with potassium cyanide and subsequent hydrolization of the dinitrile formed:



$$CH_2\left\langle\begin{array}{l} CH_2Br \\ CH_2Br \end{array}\right. \rightarrow CH_2\left\langle\begin{array}{l} CH_2CN \\ CH_2CN \end{array}\right. \rightarrow CH_2\left\langle\begin{array}{l} CH_2{\cdot}COOH \\ CH_2{\cdot}COOH \end{array}\right.$$

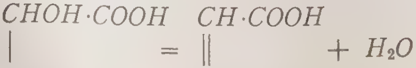
trimethylene bromide trimethylene cyanide glutaric acid

Glutaric acid crystallizes in large, colorless, monoclinic plates, is soluble in water and alcohol, melts at 98° C., and distils at about 300° C. with decomposition.

UNSATURATED DIBASIC ACIDS

33. Varieties.—Of the few dibasic acids bearing the same relation to the ethylene hydrocarbons that the oxalic acid series bear to the paraffin hydrocarbons, the most important are **fumaric acid** and **maleic acid.**

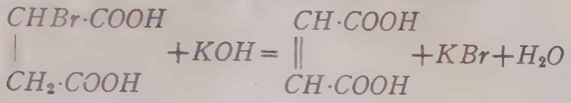
34. Fumaric Acid, $C_2H_2(COOH)_2$.—Fumaric acid occurs in many plants and may be prepared by heating malic acid which is obtained from the unripe berries of the mountain ash.



$$\begin{array}{l} CHOH{\cdot}COOH \\ | \\ CH_2{\cdot}COOH \end{array} = \begin{array}{l} CH{\cdot}COOH \\ \| \\ CH{\cdot}COOH \end{array} + H_2O$$

malic acid fumaric acid

Fumaric acid is also prepared by boiling an aqueous solution of monobrom succinic acid with caustic potash:



$$\begin{array}{l} CHBr\cdot COOH \\ | \\ CH_2\cdot COOH \end{array} + KOH = \begin{array}{l} CH\cdot COOH \\ \| \\ CH\cdot COOH \end{array} + KBr + H_2O$$

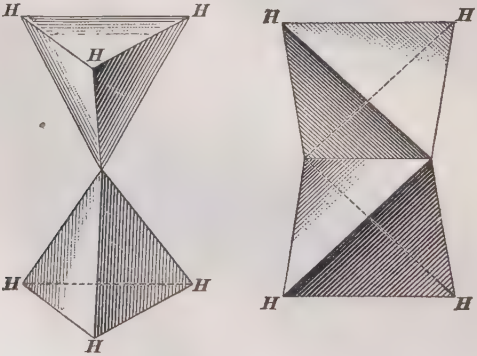
Fumaric acid is a white solid, crystallizing from hot water in small striated prisms. It does not melt at ordinary pressure, but sublimes at 200° C., and at a higher temperatures decomposes into maleic anhydride and water.

The silver salt of fumaric acid, $C_4H_2O_4Ag_2$, is insoluble in water, explodes when heated, and resists to a great extent the action of light. *Barium fumarate*, $C_4H_2O_4Ba\cdot 3H_2O$, crystallizes in efflorescent prisms, which on boiling lose their water of crystallization and become practically insoluble in water.

35. Maleic Acid, $C_2H_2(COOH)_2$.—Maleic acid is isomeric with fumaric acid. It is not a natural product, but is obtained by the heating of malic acid or by the action of silver or sodium on dichloracetic acid. In addition to these methods it is also prepared by heating fumaric acid. Its formation by heating malic or fumaric acid consists of two distinct steps. When these acids are heated maleic anhydride and water distil over, and the anhydride readily takes up water, regenerating the acid. This method of formation indicates that both fumaric acid and maleic acid have the same structural formula, $COOH\cdot CH:CH\cdot COOH$ Whether fumaric or maleic acid will be formed when malic acid is heated, depends upon the degree of heat used. Thus, if a temperature of 140° to 150° C. is maintained for some time, fumaric acid is formed, while if a higher temperature is employed and the heating is quickly carried out, maleic acid results.

Maleic acid forms large, colorless prisms, or plates, melts at 136° C., boils at 160° C., and has a peculiar, disagreeable taste. It is soluble in water and alcohol. When boiled at 160° C., it decomposes into maleic anhydride and water. Nascent hydrogen reduces both fumaric acid and maleic acid to succinic acid, and hydrobromic acid converts them into bromsuccinic acid.

36. Stereoisomerism.—The explanation of the isomerism of fumaric and maleic acids requires an extension of the principles of stereochemistry. According to the fundamental idea of stereochemistry, when a carbon atom is in combination with four different atoms or groups, it holds these atoms or groups by bonds directed toward the solid angles of a tetrahedron, the carbon atom being at the center of the tetrahedron. When two carbon atoms unite in the simplest way, the compound consists of two tetrahedrons united at one of the solid angles of each, or are singly linked, as shown in Fig. 1 (*a*). When two carbon atoms are united by a double bond, as in the ethylene compounds, two tetrahedrons are united by one of the edges, or are doubly linked, as shown in Fig. 1 (*b*).

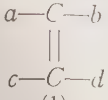


(*a*)
Single linking
$H_3C—CH_3$

(*b*)
Double linking
$H_2C=CH_2$

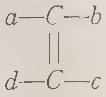
FIG. 1

If each carbon atom is in combination with two unlike atoms or groups, there are two possible ways of arrangement in space on the plane of the paper, thus;



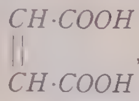
$$\begin{array}{c} a—C—b \\ \| \\ c—C—d \end{array}$$

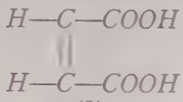
(1)



$$\begin{array}{c} a—C—b \\ \| \\ d—C—c \end{array}$$

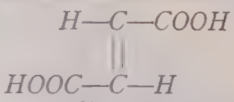
(2)

Here it will be seen that in (1), *a* and *c* are on one side and *b* and *d* are on the other side; and that in (2), *a* and *d* are on one side and b and c are on the other side. It will be seen from the ordinary formula of fumaric and maleic acids,  $\begin{array}{l} CH\cdot COOH \\ \| \\ CH\cdot COOH \end{array}$, that each carbon atom is in combination with two different atoms or groups, which can be arranged in two ways, thus:



$$\begin{array}{c} H—C—COOH \\ \| \\ H—C—COOH \end{array}$$

(3)



$$\begin{array}{c} H—C—COOH \\ \| \\ HOOC—C—H \end{array}$$

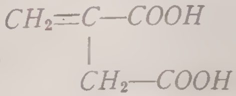
(4)

Formula (3) is the *plane-symmetrical*, or *cis-*, formula, and formula (4) is the *axial-symmetrical*, *centri-symmetrical*, or *trans-*, formula.

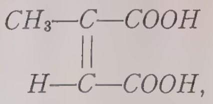
37. It now becomes necessary to show which of the formulas in the preceding article belongs to fumaric acid and which to maleic acid. When maleic acid is heated it loses water and forms an anhydride, but under the same conditions, fumaric acid does not form an anhydride. Since an anhydride is formed by the interaction of the two carboxyl groups, these groups must be close together. In (3), the carboxyl groups are closer to each other than they are in (4), hence this must be the formula for maleic acid, and the trans-formula that for fumaric acid.

38. Itaconic, Citraconic and Mesaconic Acids.—Among the acids of the olefine series are the three isomeric dibasic acids of the formula $C_3H_4(COOH)_2$, namely, itaconic acid, citraconic acid, and mesaconic acid.

Itaconic acid and citraconic acid are prepared by heating citric acid. By dehydration, both are converted into citraconic anhydride, and when this is heated at 150° C. with water, itaconic acid is again formed.

Itaconic acid,  $\begin{array}{l} CH_2{=}C—COOH \\ \quad\;\; | \\ \quad\;\; CH_2—COOH \end{array}$, or methylene succinic acid, forms trimetric, octahedral crystals, is strongly acid, melts at 161° C., and is soluble in water, alcohol, and ether. Nascent hydrogen reduces it to pyrotartaric acid.

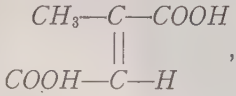
Citraconic acid,



$$\begin{array}{l}CH_3\text{—}C\text{—}COOH\\ \quad\;\;\;\; \|\\ \;\;H\text{—}C\text{—}COOH,\end{array}$$

or methyl maleic acid, crystallizes in yellowish, four-sided prisms; it has a specific gravity of 1.60 and melts at 80° C. It is more soluble in water than itaconic acid, and is also soluble in alcohol and ether. Hydrogen has the same effect on this acid as it does on itaconic acid

Mesaconic acid,



$$\begin{array}{l}\quad\;\;CH_3\text{—}C\text{—}COOH\\ \qquad\qquad\;\; \|\\ COOH\text{—}C\text{—}H\end{array}$$

, or methyl fumaric acid, is formed by the oxidation of citraconic anhydride with nitric acid. It is a colorless, crystalline powder, soluble in alcohol and ether, sparingly soluble in water, and melts at 202° C.

MONOHYDROXY DIBASIC ACIDS

39. Introductory.—The monohydroxy dibasic acids bear the same relation to the dibasic acids of the oxalic-acid series as do the simplest hydroxy acids to the acids of the formic-acid series. The most important acids of this series are tartronic and maleic acids.

40. Tartronic Acid, $CH(OH)(COOH)_2$.—Tartronic acid, or hydroxy malonic acid, is obtained when monobrom malonic acid is treated with silver hydroxide. Thus,

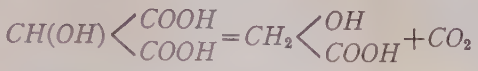
$$CHBr\!<\!\begin{array}{l}COOH\\COOH\end{array}+AgOH=CH(OH)\!<\!\begin{array}{l}COOH\\COOH\end{array}+AgBr$$

It is also obtained by the action of caustic potash on bromcyanacetic acid; thus,

$$CHBr\!<\!\begin{array}{l}CN\\COOH\end{array}+2KOH+H_2O$$

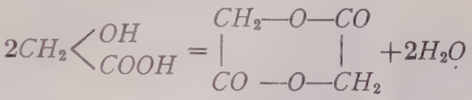
$$=CH(OH)\!<\!\begin{array}{l}COOK\\COOH\end{array}+NH_3+KBr$$

Tartronic acid is a white to yellowish solid that crystallizes in prisms. It is soluble in water and alcohol. The crystals melt at 184° C., giving off water and carbon dioxide, forming glycolide. This reaction occurs in two steps; in the first the tartronic acid loses carbon dioxide and forms glycolic acid; thus,



$$CH(OH)\Big\langle\begin{array}{l}COOH\\COOH\end{array} = CH_2\Big\langle\begin{array}{l}OH\\COOH\end{array} + CO_2$$

In the second, the glycolic acid thus formed loses water and at once yields the glycolide; thus,



41. Malic Acids, $C_2H_3(OH)(COOH)_2$.—Three varieties of malic acid are known. The most important is ordinary malic acid, $\begin{array}{l}CH(OH)\cdot COOH\\ | \\ CH_2\cdot COOH\end{array}$, or *levo-malic acid,* which is found in various unripe fruits and is best prepared from the unripe berries of the mountain ash. It was first extracted from apple juice by Scheele in 1785. It is extracted as the calcium salt from the berries of the mountain ash by pressure and boiling with milk of lime, and is then purified by crystallization.

Malic acid is a colorless, crystalline solid with an agreeable sour taste. It is readily soluble in alcohol and water and melts at 100° C. When heated to 140° C. it loses water and is converted into fumaric acid; if heated to 180° C. it forms maleic acid.

When ordinary malic acid is treated with hydriodic acid it is reduced to succinic acid. Although malic acid is hydroxy succinic acid, if bromsuccinic acid is treated with moist silver oxide instead of the *l*- or ordinary malic acid being obtained, the inactive malic acid results.

42. *Inactive malic acid,* $C_2H_3(OH)\Big\langle\begin{array}{l}COOH\\COOH\end{array}$, results when bromsuccinic acid is treated with moist silver oxide. It can also be made by reducing racemic acid, and by heating fumaric acid with water. The properties of *i*- malic acid are very similar to those of the ordinary malic acid; in fact, their chemical properties are practically identical. Their principal difference, as in the case of lactic acid, is their action toward polarized light. When inactive malic acid is treated with cinchonine it is resolved into salts of the *d*- and *l*-varieties.

Dextro-malic acid was first prepared by Bremer by the reduction of ordinary or *d*-tartaric acid.

DIHYDROXY DIBASIC ACIDS

43. Mesoxalic Acid, $(OH)_2C \cdot (COOH)_2$.—Mesoxalic acid or dihydroxy malonic acid is made by treating monobrom malonic acid with a solution of barium hydroxide. It is also found as an important decomposition product of uric acid. It crystallizes in deliquescent prisms that melt at 115° C. without the loss of water. At higher temperatures it evolves carbon dioxide and glyoxylic acid, $COOH \cdot CHO$. The aqueous solution on evaporation breaks up into carbon dioxide and oxalic acid. This acid is an example of a very rare condition, as it appears to be a compound in which two hydroxyls are in combination with the same carbon atom. The exact structure of mesoxalic has not yet been established.

44. Tartaric Acids, $C_2H_2(OH)_2(COOH)_2$.—Tartaric acid or dihydroxy succinic acid exists in four isomeric forms. They are *dextro-*, or *ordinary, tartaric acid*, *levo-tartaric acid*, racemic acid, and mesotartaric acid. Their constitutional formula is $COOH \cdot CHOH \cdot CHOH \cdot COOH$ and shows the presence of two asymmetric carbon atoms.

Ordinary, or dextrotartaric acid is one of the most widely distributed vegetable acids. It occurs in fruits, either as the potassium or calcium salt, and can be prepared by the oxidation of sugar of milk by means of nitric acid, or by the oxidation of cane sugar, starch, and similar substances. It has been prepared synthetically by boiling the silver salt of dibromsuccinic acid with water. Its principal source is from tartar, the deposit formed on the sides and bottoms of casks in which wine is manufactured. This acid potassium tartrate is purified by crystallization and the acid is neutralized with chalk, when an almost insoluble calcium tartrate is precipitated. This is then decomposed by sulphuric acid, the free tartaric acid being allowed to crystallize from the concentrated solution.

Tartaric acid crystallizes in colorless, transparent, rhombic crystals that are soluble in water and alcohol, have a specific gravity of 1.76, and melt at 170° C. The aqueous solution of these crystals turn the plane of polarized light to the right. Hydriodic acid first reduces tartaric acid to maleic acid and then to ordinary succinic acid; thus,

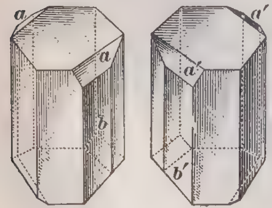
$$C_2H_2(OH)_2\cdot(COOH)_2+2HI=\underset{\text{maleic acid}}{C_2H_3(OH)\cdot(COOH)_2}+H_2O+I_2$$

$$C_2H_3(OH)(COOH)_2+2HI=\underset{\text{succinic acid}}{C_2H_4(COOH)_2}+H_2O+I_2$$

45. Salts of Tartaric Acid.—Tartaric acid forms many important salts known as *tartrates*. *Hydropotassium tartrate*, $KH\cdot C_4H_4O_6$, or *monopotassium tartrate*, forms the chief constituent of tartar, and in its pure form is known as *cream of tartar*. It is prepared by recrystallizing argol from hot water, which dissolves about $\frac{1}{15}$ of its weight, but retains only $\frac{1}{200}$ on cooling. It crystallizes in small slightly translucent, or transparent, prismatic crystals, has a decided sour taste and an acid reaction. It is nearly insoluble in water, but dissolves readily in acids and alkalies. Caustic potash converts into it the *normal potassium tartrate*, $K_2C_4H_4O_6$. *Sodium potassium tartrate*, $KNaC_4H_4O_6+4H_2O$, finds great use in medicine as a purgative under the name of *Rochelle salt*. It is frequently called *Seignette salt*, as it was discovered by Seignette in 1672. It crystallizes in beautiful, large, colorless, rhombic prisms, is used in Seidlitz powders, has a mild saline taste, and melts at 74° C. *Calcium tartrate*, $CaC_4H_4O_6+4H_2O$, is found in grapes and in senna leaves. It is usually precipitated from solutions of the neutral tartrates by calcium chloride in the form of an insoluble crystalline substance. It serves to distinguish tartaric acid from other acids in that it is soluble in acids and alkalies, but is reprecipitated as a jelly on boiling. *Cupric tar-*

trate, $CuC_4H_4O_6+3H_2O$, is important as the alkaline solution, known as *Fehling's solution*, used for the detection and determination of sugar. It is only sparingly soluble in water. *Potassium antimonyl tartrate*, $K(SbO)\cdot C_4H_4O_6$, or *tartar emetic*, is prepared by digesting cream of tartar with antimonic oxide. It forms transparent rhombic octahedrons that slowly lose their water of crystallization, becoming a white, opaque powder. It has a sweet, unpleasant, metallic taste.

46. Racemic Acid.—Racemic acid is isomeric with tartaric acid and occurs with it in many kinds of grapes and in the crude tartar. In recrystallizing cream of tartar, the acid potassium racemate, being more soluble than the tartrate, remains in the mother liquor. It can be prepared by oxidizing mannitol with nitric acid, or by oxidizing fumaric acid with potassium permanganate. Racemic acid, together with some mesotartaric acid, is formed when ordinary tartaric acid is heated to 175° C. with water. It is also prepared by mixing equal quantities of the concentrated solutions of *d*- and *l*-tartaric acids. Crystals of natural racemic acid differ from the synthetic acid by not disintegrating on exposure to air. It crystallizes with one molecule of water. The crystals effloresce in the air and become completely anhydrous at 100° C.; they melt at 200° C. Racemic acid is less soluble than tartaric acid. Its solutions are optically inactive.



(a) (b)

FIG. 2

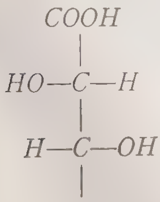
47. Salts of Racemic Acid.—Calcium racemate, $CaC_4H_4O_6+4H_2O$, is formed when solutions of *d*- and *l*- calcium tartrates are mixed. It is characterized by being less soluble in water than the calcium tartrate, and is insoluble in acetic acid and ammonium chloride. The *acid potassium racemate* is considerably more soluble than the cream of tartar. If a solution of *sodium ammonium racemate*, $NaNH_4C_4H_4O_6$, is allowed to evaporate in the air large crystals are deposited, which, on examination, are found to consist of two kinds. Some of these crystals have certain hemihedral faces developed, and others have the complementary hemihedral faces, one kind of crystals being practically the mirror image of the other kind. These different crystals are said to be *enantiomorphous* and are shown in Fig. 2. When the crystals are separated and each kind is dissolved in equal quantities of water, those having the right-handed hemihedral faces shown in (*a*) will be found to turn the plane of polarized light to the right, and those having the left-handed hemihedral faces shown in (*b*) will turn the plane of polarized light to the left.

When separated, the acids of these salts will be found to have the same action on polarized light. The acid obtained from the right-handed crystals is ordinary *d*- tartaric acid, and the acid from the left-handed crystals is the isomeric *l*- tartaric acid. Solutions of equal weights of these two acids when brought together, unite with an evolution of heat and racemic acid is formed. This reaction shows that the optically inactive racemic acid is composed of two optically active substances in combination, one of which is dextrorotatory, and the other levorotatory.

48. Mesotartaric Acid.—Mesotartaric acid, or inactive tartaric acid, is very similar to racemic acid. It is produced by boiling *d*- tartaric under a reflux condenser with a large excess of caustic soda; or *d*- tartaric acid is heated for some time to 165° C., with a small quantity of water. It is optically inactive, as its name implies, but cannot be resolved into two acids. It is also obtained when dibromsuccinic acid is treated with moist silver oxide. Mesotartaric acid is very soluble in water and crystallizes in rectangular tables containing one molecule of water. It forms an acid potassium salt, which is more soluble than the corresponding salt of ordinary tartaric acid, and which does not crystallize. Calcium mesotartrate is obtained first as a flocculent precipitate, which soon becomes crystalline, containing three molecules of water of crystallization. It is more soluble than the calcium tartrate and when heated to 170° C. is converted into *d*-tartaric acid.

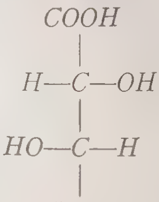
49. Levotartaric Acid.—Levotartaric acid and its salts are all very similar to *d*- tartaric acid and its salts. It forms anhydrous, hemihedral rhombic crystals, whose aqueous solution turns the plane of polarized light to the left This rotation is equal and opposite to that produced by the *d*-tartaric acid. It ferments less readily than the *d*- variety and unites with it to form racemic acid.

50. Stereoisomerism.—It has already been explained that racemic acid can be broken up into two optically active acids, namely, *d*-, and *l*-, tartaric acids, but that the inactive mesotartaric acid cannot be so divided; also that a combination of the two optically active acids forms the inactive racemic acid. Hence, as it is generally expressed, racemic acid is an externally compensated compound, while mesotartaric acid is inactive because it is an internally compensated compound. Therefore, an externally compensated compound is one that is optically inactive because it is composed of two opposite optically active compounds, and an internally compensated compound is one that is incapable of being separated into two optically active compounds and that contains the different radicals grouped about the asymmetric carbon atom in such a manner that the compound is optically inactive. The phenomenon of these compounds is best explained by reference to the formulas here given. The tartaric acids contain two asymmetric carbon atoms, and if the groups and atoms be arranged in the same way about both of the carbon atoms, the compound will be optically active, being either *d*-, or *l*-, rotatory.



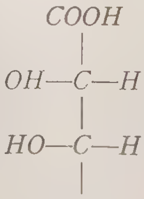
$$\begin{array}{c} COOH \\ | \\ HO—C—H \\ | \\ H—C—OH \\ | \\ COOH \end{array}$$

l-tartaric acid



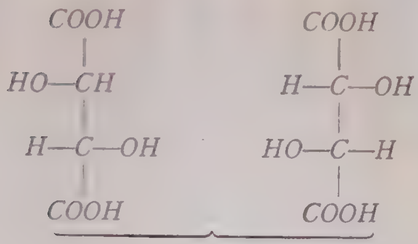
$$\begin{array}{c} COOH \\ | \\ H—C—OH \\ | \\ HO—C—H \\ | \\ COOH \end{array}$$

d-tartaric acid



$$\begin{array}{c} COOH \\ | \\ OH—C—H \\ | \\ HO—C—H \\ | \\ COOH \end{array}$$

internally compensated or mesotartaric acid



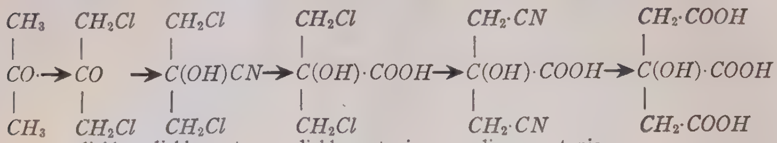
$$\underbrace{\begin{array}{c}COOH\\|\\HO-CH\\|\\H-C-OH\\|\\COOH\end{array}\qquad\begin{array}{c}COOH\\|\\H-C-OH\\|\\HO-C-H\\|\\COOH\end{array}}$$

externally compensated tartaric acid, or racemic acid

If arranged in the opposite manner about both asymmetric carbon atoms, the complementary stereoisomeric form will result. A combination of these two optically active forms will give the externally compensated inactive form. On the other hand, if the groups are arranged in one way about the one asymmetric carbon atom and in the other way around the other asymmetric carbon atom, the resulting compound will be the internally compensated, or mesotartaric, acid, and will be incapable of resolution into two active modifications.

MONOHYDROXY TRIBASIC ACIDS

51. Citric Acid, $C_3H_4(OH)(COOH)_3$.—Citric acid is the only monohydroxy tribasic acid of sufficient importance to be treated here. It is found very widely distributed in nature in many fruits, especially in the lemon, in which it occurs free. It is prepared by treating lemon juice with lime, the calcium salt formed, subsequently being decomposed by means of sulphuric acid. Citric acid is also prepared on a large scale by the fermentation of glucose. The particular ferments employed are fungi or molds called *citromycetes*, which are developed for use by permitting a solution of sugar that contains about 3 per cent. of citric acid, to stand in contact with air for a few days. The action of the ferment, when introduced into a solution of glucose, is to split up the latter into citric acid and carbon dioxide. About 50 per cent. of the glucose is converted to citric acid in the process. Citric acid can also be prepared synthetically from acetone by the following steps, the formulas of the principal products formed by each reaction being given; thus,



$$\begin{array}{ccccccccccc} CH_3 & & CH_2Cl & & CH_2Cl & & CH_2Cl & & CH_2\cdot CN & & CH_2\cdot COOH \\ | & & | & & | & & | & & | & & | \\ CO & \rightarrow & CO & \rightarrow & C(OH)CN & \rightarrow & C(OH)\cdot COOH & \rightarrow & C(OH)\cdot COOH & \rightarrow & C(OH)\cdot COOH \\ | & & | & & | & & | & & | & & | \\ CH_3 & & CH_2Cl & & CH_2Cl & & CH_2Cl & & CH_2\cdot CN & & CH_2\cdot COOH \end{array}$$

acetone; dichlor acetone; dichloracetone cyanhydrate; dichloracetonic acid; dicyanacetonic acid; citric acid

52. Properties.—Citric acid crystallizes in colorless rhombic crystals containing one molecule of water. It is odorless but very acid. It is permanent in dry air, at ordinary temperatures, but is rather efflorescent in warm air; it deliquesces in moist air, and is soluble in water and alcohol. The anhydrous acid melts at 153° C. Heated at 170° C., citric acid loses water and yields aconitic acid; this is shown by the equation.

$$C_3H_4(OH)(COOH)_3 = C_3H_3\cdot(COOH)_3 + H_2O$$

When fused with caustic potash or oxidized by nitric acid, it breaks down into acetic acid and oxalic acid. Heated above 175° C., citric acid first yields aconitic acid, then evolves carbon dioxide, forming itaconic anhydride, which, on further heating, is partly converted into citraconic anhydride.

Citric acid is frequently adulterated with tartaric acid. The presence of the latter acid can be readily detected by adding a small quantity of potassium acetate to the aqueous solution, when a white, crystalline precipitate of cream of tartar is produced if tartaric acid is present. Lime water does not give a precipitate with citric acid in cold solutions, but, on boiling, tricalcium citrate is precipitated; this is insoluble in caustic potash.

53. Salts of Citric Acid.—The salts of citric acid are known as *citrates*. Those which it forms with the alkalies are readily soluble, but nearly all those of the heavier metals are insoluble. *Ferric citrate*, $Fe_2(C_6H_5O_7)_2\cdot 6H_2O$, is used in medicine as a tonic. It occurs as reddish-brown scales, very slowly soluble in cold water, soluble in hot water, but insoluble in alcohol. *Ferric ammonio citrate*, $Fe_2(NH_4)_3(C_6H_5O_7)_3$, is used in medicine and also in the manufacture of blueprints. It forms reddish-brown, transparent, hygroscopic scales, having a saline, ferruginous taste, deliquescing in moist air. The *monopotassium citrate*, $KH_2 \cdot C_6H_5O_7 \cdot 2H_2O$, occurs as a white crystalline powder soluble in water. The *tripotassium citrate*, $K_3 \cdot C_6H_5O_7 \cdot H_2O$, is also used medicinally. It is a colorless, crystalline mass with a cooling, saline taste. It is soluble in water and alcohol, and decomposes at 230° C. These last two salts, together with the *dipotassium citrate*, $K_2H \cdot C_6H_5O_7$, are made by mixing citric acid and potassium carbonate in the proper proportions.

Calcium citrate, $Ca_3(C_6H_5O_7)_2 \cdot 4H_2O$, is obtained by mixing an alkali citrate with calcium chloride. It forms white crystals that are more soluble in cold water than in hot, hence, boiling causes a precipitate. *Magnesium citrate*, $Mg_3(C_6H_5O_7)_2 \cdot 14H_2O$, prepared by dissolving magnesia in citric acid, forms white scales having a feeble saline taste. It is readily soluble in water, and is used in medicine.

CARBOHYDRATES

CLASSIFICATION AND NOMENCLATURE

54. The carbohydrates comprise a large class of compounds, including the natural sugars, widely distributed in nature. The name was originally given to these compounds because they consist of carbon, hydrogen, and oxygen in such proportions that if all the hydrogen and oxygen were removed in the form of water only carbon would remain. The carbohydrates are aldehydo alcohols and keto alcohols; they contain several hydroxyl groups and one carbonyl group. One of the hydroxyl groups must be linked directly to a carbon atom in union with the carbonyl group. The characteristic group of these compounds is $—CHOH—CO—$.

The carbohydrates are divided into two main classes namely, monosaccharoses and polysaccharoses. The monosaccharoses are the simplest carbohydrates. They are further subdivided into eight classes depending upon the number of carbon atoms they contain. Thus there are bioses, $C_2H_4O_2$; trioses, $C_3H_6O_3$; tetroses, $C_4H_8O_4$; pentoses, $C_5H_{10}O_5$; hexoses, $C_6H_{12}O_6$; heptoses, $C_7H_{14}O_7$; octoses, $C_8H_{16}O_8$; and nonoses, $C_9H_{18}O_9$. The monosaccharoses are also designated as aldoses or ketoses, depending upon whether they contain the aldehyde group or the ketone group. Thus it is possible to have an aldo-pentose and a keto-pentose, which are structurally isomeric.

Since the monosaccharoses are the simplest carbohydrates, it is impossible to split them up into simpler carbohydrates or sugars by hydrolysis. In the second main division into which the carbohydrates are divided, the polysaccharoses, further subdivision also exists. Thus there are disaccharoses, or hexobioses having the formula $C_{12}H_{22}O_{11}$; and trisaccharoses or hexotrioses having the formula $C_{18}H_{32}O_{16}$. From these formulas it is seen that hexose is regarded as the principal unit sugar from which all of the polysaccharoses are theoretically derived. On the hydrolysis of the disaccharoses, two molecules of the monosaccharose, hexose, are obtained, while hydrolysis of a trisaccharose yields three molecules of the monosaccharose.

The third main class of carbohydrates, the higher polysaccharoses, are not true sugars. On hydrolysis, the number of molecules of the monosaccharose formed, depends on the number of carbon atoms in the polysaccharose.

MONOSACCHAROSES

ALDEHYDE AND KETO ALCOHOLS

55. When the monohydroxy primary alcohols are acted upon by oxidizing agents, the first product formed is an aldehyde; when a monohydroxy secondary alcohol is oxidized, the first product is a ketone. In a similar manner, when an alcohol containing more than one OH group is oxidized, the product formed will be an aldehyde or ketone, depending on whether the particular alcohol group acted on is a primary or secondary one. Therefore, by means of reactions of this type, it is possible to obtain compounds which contain the hydroxyl group, characteristic of an alcohol, together with either an aldehyde or ketone group.

BIOSES, TRIOSES, AND TETROSES

56. Glycolic Aldehyde, $CH_2OH \cdot CHO$.—Glycolic aldehyde which, because of its structure, is classed as a biose, is obtained when ethylene glycol is oxidized.

$$CH_2OH \cdot CH_2OH + O = CH_2OH \cdot CHO + H_2O$$

It is not a true sugar and does not possess the general properties of the sugars, although it contains the alcohol and aldehyde group which is characteristic of them.

57. Glycerose.—Glycerose, a triose, is obtained when the trihydroxy alcohol, glycerol, is oxidized, and since the alcohol contains both a primary and secondary OH group, both an aldehydo alcohol, *glyceric aldehyde*, $CH_2OH \cdot CHOH \cdot CHO$, and a keto alcohol, *dihydroxy acetone*, $CH_2OH \cdot CO \cdot CH_2OH$ are obtained. It is this mixture which is known as *glycerose*. The equations that represent the reaction which takes place are written as follows:

$$CH_2OH \cdot CHOH \cdot CH_2OH + O = CH_2OH \cdot CHOH \cdot CHO + H_2O$$
$$CH_2OH \cdot CHOH \cdot CH_2OH + O = CH_2OH \cdot CO \cdot CH_2OH + H_2O$$

Glycerose responds to the two general tests by which carbohydrates and sugars are distinguished from other compounds, in that it is fermentable, alcohol being formed, and it precipitates red cuprous oxide from an alkaline tartrate solution of copper sulphate. This solution is known as *Fehling's solution* and is used in the quantitative determination of the sugars.

58. Erythrose, $C_4H_8O_4$.—Erthyrose, a tetrose, may be obtained by oxidizing the tetrahydroxy alcohol erythritol. The reaction is analogous to that which takes place when glycerol is oxidized in the preparation of glycerose. Erythrose is also obtained when the calcium salt of pentonic acid is oxidized with hydrogen peroxide. Thus,

$$Ca[(CH_2OH)\cdot(CHOH)_3COO]_2+2H_2O_2=2CH_2OH(CHOH)_2CHO$$
$$+CaCO_3+3H_2O+CO_2$$

The reaction is accelerated if a small quantity of ferric acetate, which acts as a catalyst, is present.

Erythrose is not fermentable. When strongly oxidized, tartaric acid is formed.

$$CH_2OH(CHOH)_2CHO+O_2=(CHOH)_2(COOH)_2$$

PENTOSES

59. Formation of Pentoses.—The pentoses may be formed by oxidizing the calcium salt of hexonic acid with hydrogen peroxide. Thus,

$$Ca[(CH_2)HO(CHOH)_3CHOH\cdot COO]_2+2H_2O_2$$
$$=2CH_2OH(CHOH)_3CHO+CaCO_3+CO_2+3H_2O$$

A number of pentoses are known; the most important are arabinose, $C_5H_{10}O_5$; xylose, $C_5H_{10}O_5$; and rhamnose, $C_6H_{12}O_5$. These are the lowest well-known members of the monosaccharides and occur in many plants as polyoses, called pentosans. The first two are aldoses, or aldehydo alcohols.

60. Arabinose, $C_5H_{10}O_5$.—Arabinose is prepared from gum arabic or cherry gum by boiling these substances with dilute sulphuric acid. It has a sweet taste and is dextrorotatory. Arabinose forms well-defined crystals that melt at 160° C.

61. Xylose, $C_5H_{10}O_5$.—Xylose or wood sugar is obtained by boiling wood, bran, or straw with dilute acids. It forms crystals that melt at temperatures between 140° C. and 160 C.° It is dextrorotatory.

62. Rhamnose, $C_6H_{12}O_5$.—Rhamnose is obtained by boiling quercitrin, obtained from black-oak bark, with dilute sulphuric acid. When anhydrous it melts at 93° C. It has a sweet taste and is dextrorotatory. Rhamnose is the methyl derivative of a pentose and hence should have the structural formula $CH_3\cdot C_5H_9O_5$.

HEXOSES

63. Glucose, $C_6H_{12}O_6$.—Glucose, also called *dextrose* and *grape sugar*, occurs in honey, in sweet fruits, and in the urine of persons afflicted with diabetes mellitus.

Glucose may be prepared by the hydrolysis of cane sugar, and is also extracted from fruits by crushing them and digesting the pulp with water. The solution thus obtained is boiled to coagulate the albumin that it contains, and after filtration the clear liquid is concentrated by evaporation and then allowed to cool. Crystals are deposited from the cold concentrated solution.

Glucose is prepared on a large scale from corn starch which is boiled with an excess of dilute sulphuric acid, the excess acid being subsequently removed by neutralization with lime and filtration of the calcium sulphate formed. The clear solution obtained is then either evaporated to a syrup forming the glucose, or mixing syrup of commerce, or it is evaporated to dryness and sent to the market as grape sugar.

Glucose crystallizes from water in small, white nodules containing one molecule of water of crystallization, and melts at 86° C. At 110° C. it loses its water of crystallization, forming a mass very much resembling granulated sugar. Crystallized from methyl alcohol, it contains no water of crystallization and melts at 146° C. It is soluble in water, dissolving in about its own weight. It is much less soluble in alcohol than in water, and is only about one-half as sweet as cane sugar.

Glucose is dextrorotatory. It is fermentable by yeast, with the formation of alcohol and carbon dioxide. Silver and copper are reduced by it to the metallic state from solutions of their salts. Advantage is taken in testing urine for glucose of its action toward alkaline solutions of copper tartrate. A few cubic centimeters of Fehling's solution is added to the suspected urine and the mixture boiled. If glucose is present, a red precipitate of cuprous oxide is formed. Glucose is largely used in the manufacture of confectionery and alcohol.

64. Levulose, $C_6H_{12}O_6$.—Levulose, also called *fructose*, or *fruit sugar*, occurs with glucose in most sweet fruits. It is a ketose, of which but few are known, and has the formula $CH_2OH \cdot (CHOH)_3 \cdot CO \cdot CH_2OH$. It is formed by the action of dilute mineral acids on cane sugar. *Inulin* obtained from dahlia tubers yields pure levulose on hydrolyzation just as starch yields glucose. It is separated from glucose, when obtained by the decomposition of cane sugar, by the insolubility of its calcium compound.

Levulose is levorotatory. It crystallizes with difficulty owing to its solubility in water. It is sweeter than glucose, and is sometimes used as a substitute for cane sugar in cases of diabetes. Levulose is fermentable and reduces Fehling's solution.

65. Galactose, $H_6H_{12}O_6$.—Galactose is prepared by the hydrolysis of lactose or milk sugar. It crystallizes in rhombic prisms, melts at 168° C., and is less sweet than cane sugar. It is soluble in water, sparingly soluble in alcohol, and undergoes fermentation.

DISACCHAROSES

66. Important Members.—The disaccharoses of greatest importance are sucrose, or cane sugar; maltose, or malt sugar; and lactose, or milk sugar. They are all derived from natural sources. All are capable of breaking down into monosaccharoses either by boiling with dilute acids, or by the action of enzymes.

67. Sucrose, $C_{12}H_{22}O_{11}$.—Sucrose, which is more commonly known as *cane sugar*, occurs widely distributed in nature in the juice of many plants. It occurs chiefly in sugar cane, in some varieties of maple, and in beet roots. It is obtained on a large scale mainly from sugar cane and from beet roots, the former containing about 20 per cent., and the latter from 10 to 20 per cent. of sugar.

68. Manufacture of Cane Sugar.—In the manufacture of sucrose from sugar cane or from the sugar beet, the cane is reduced to fine shreds or the beet is sliced and either material is then introduced into a series of cylindrical iron vessels called *diffusers*, in which it is brought in contact with water. The operation of the diffusers is carried on in such a way that the almost exhausted material in the first diffuser is brought in contact with fresh water, while the last diffuser in the series contains fresh material which is brought in contact with a solution of sucrose that is already fairly strong. In this manner practically all of the sugar is extracted from the nearly exhausted material and as the solution passes through each diffuser in turn it meets with fresher and fresher material and its sucrose content gradually increases. When the material in the first diffuser has been exhausted it is emptied and charged with fresh material. It then becomes the last diffuser in the series and what was the second diffuser now becomes the first.

From the last diffuser the sucrose solution goes to the defecators which are merely cylindrical, round-bottomed, steam-heated kettles. In the defecators the sugar solution is heated with lime. The heat coagulates the albumin, which makes it easier to remove, and the lime precipitates oxalic and citric acids and other substances that may be present. When the operation has been properly carried out, the precipitate formed will settle on the bottom of the defactor in the form of mud. The clear solution of sucrose and calcium sucrate is then drawn off and the lime present as sucrate is precipitated as carbonate by the introduction of carbon dioxide. This treatment also removes the mechanical impurities that are carried to the bottom of the tank by the calcium carbonate, and most of the coloring matter. The solution at this point has a bright amber color.

The solution is now pumped into the sulphuring tanks where sulphur dioxide is passed through it. The last traces of lime are removed in this manner and the solution is completely decolorized. It is now filtered, then concentrated under diminished pressure and, upon being allowed to cool, the sucrose crystallizes. Most of the mother liquor is removed from the crystals by centrifuging and the product obtained is then subjected to further refining processes if necessary. To remove the last traces of color and other impurities, the crude sugars are redissolved in water, the solution filtered through charcoal, then concentrated, and the sucrose crystallized as before.

69. Properties of Sucrose.—Sucrose crystallizes from water in large, monoclinic prisms. It is very soluble in water, but dissolves with difficulty in alcohol. It has a specific gravity of 1.606 and is dextrorotatory. It melts at 160° C. and on cooling solidifies to an amorphous, glass-like mass, which in time again becomes crystalline and nontransparent. Heated to 220° C., it loses water and turns brown, being converted into caramel, a substance used extensively as a coloring agent. Sucrose with dilute mineral acids breaks up into equal parts of glucose and fructose; the mixture is called *invert sugar*, and the process is known as *inversion*. Invert sugar is levorotatory. As this process takes place, to some extent, when impure sugars are allowed to stand, the brown sugars of commerce contain some invert sugar. Although sucrose itself does not ferment, yeast gradually transforms it into glucose and fructose, and these undergo fermentation.

Oxidizing agents convert sucrose into oxalic acid and saccharic acid. It forms compounds, with the alkalies and the bases, known as *sucrates*.

Sucrose, although composed of a molecule of glucose and one of fructose, does not reduce Fehling's solution, neither does it react with phenylhydrazine. Hence, it is evident that there are no free carbonyl groups in the molecule, and the two monosaccharoses are linked together by a dicarbonyl bond $<O>$, therefore sucrose has the formula.

$$C_6H_{11}O_5<O>C_6H_{11}O_5$$

Sucrose has never been prepared artificially from glucose and fructose.

70. Lactose, $C_{12}H_{22}O_{11} \cdot H_2O$.—Lactose, or milk sugar, is found in milk to the extent of about 3 to 6 per cent. It is usually prepared from whey, which is the liquid remaining after milk has been used for making cheese. The whey is concentrated by evaporation and upon cooling, the lactose separates in the crystalline form. It is further purified by recrystallization.

Lactose crystallizes in hard, white rhombic prisms containing one molecule of water. It loses this molecule of water at 140° C., and at 205° C. melts with decomposition. It is soluble in water, insoluble in alcohol, has a slightly sweet taste, and is dextrorotatory.

Lactose reduces Fehling's solution. It does not ferment easily with yeast, but readily undergoes lactic fermentation. Hydrolysis splits it up into galactose and glucose.

71. Maltose, $C_{12}H_{22}O_{11} \cdot H_2O$.—Maltose, or malt sugar, is found in malt, which is the product obtained when any grain, particularly barley, is caused to germinate or sprout. It is formed by the action of an enzyme called *diastase*, which acts on the starch of the grain and converts it into maltose. The latter is extracted from the grain by means of water and upon evaporating the solution to a thick syrup, the maltose of commerce is obtained.

Maltose can also be obtained in the form of small needles that melt at 100° C. Its solution is dextrorotatory. It reduces Fehling's solution, but it is not fermentable by yeast. Upon hydrolysis with dilute acids, maltose is split up into two molecules of glucose.

TRISACCHAROSES

72. Raffinose, $C_{18}H_{32}O_{16}$, is the most important trisaccharose. It is found in the sugar beet and in the molasses obtained from the manufacture of sucrose.

Raffinose crystallizes in fine needles that melt at about 118° C. It is dextrorotatory and has only a slightly sweet taste. It is much more soluble in water than is sucrose and this property accounts for its accumulation in the molasses. It does not reduce Fehling's solution. Upon hydrolysis it splits up into fructose and a disaccharose called *melbiose*. The latter upon hydrolysis breaks up into glucose and galactose.

POLYSACCHAROSES

73. Properties.—Most of the polysaccharoses are insoluble in water, do not have a sweet taste, and are amorphous. They have a very high molecular weight and are considered to be made up of an unknown number of hexose molecules having the empirical formula $C_6H_{10}O_5$. The general formula for the polysaccharoses is, therefore, $(C_6H_{10}O_5)_x$, in which x represents an unknown quantity.

Upon hydrolysis or under the influence of ferments the polysaccharoses yield hexose monosaccharoses. Thus starch, glycogen, and dextrin yield glucose; cellulose yields mannose, galactose, and glucose and inulin yields fructose.

74. Starch.—Starch is found widely distributed throughout nature in cells of tubers, roots, and the seeds of many plants, in the form of circular or elongated granules varying in size in different plants. The size of the starch grains varies from .002 to .185 milligram. Potato starch is prepared by grinding the potatoes to destroy the cell tissue. The starch granules are thus laid bare and are washed with water on to sieves of silk bolting cloth kept in constant motion. These sieves retain the fibrous material and allow the starch grains to pass through with the water. On allowing the starchy liquid to settle, the starch is obtained as a sediment which, after drying, becomes the laundry starch of commerce. Corn starch is prepared in a similar manner from corn.

Starch is a white, tasteless powder insoluble in cold water, alcohol, and ether. In hot water the cells swell up and burst, yielding a partial solution, which on cooling, forms a transparent jelly of starch paste. With iodine, starch paste gives a blue coloration. Alcohol precipitates a white powder called *soluble starch* from aqueous solutions, and treatment with cold dilute mineral acids forms the same product. Boiling with dilute acids converts starch into dextrine and glucose, and diastase converts it into dextrin and maltose. Heated alone to 180° C., or with nitric acid to 110° C., starch is converted into dextrin.

75. Cellulose.—Cellulose is a polysaccharose of very high molecular weight. It forms the chief constituent of the cell membranes of all plants. Crude cellulose presents different appearances and properties, depending on the source from which it is obtained, and the substances with which it is mixed.

Pure cellulose may be obtained by treating the plant fiber successively with dilute caustic potash, oxidizing agents, and water. This leaves the cellulose as a white amorphous mass.

Pure cellulose is insoluble in all ordinary solvents, and is very stable toward dilute acids, and alkalies. It dissolves in an ammoniacal copper solution, called *Schweitzer's reagent*, from which various salts of alkalies, and sugar precipitate it. It dissolves also in a warm, concentrated, aqueous solution of zinc chloride. Subjected to dry distillation, cellulose leaves a residue of carbon and yields numerous gaseous and liquid products similar to those obtained by the distillation of wood. Concentrated sulphuric acid attacks cellulose, causing it to swell and dissolve, yielding a paste from which water precipitates a body analogous to starch, called *amyloid*, which is colored blue by iodine Dilute sulphuric acid on boiling with this substance converts it first into dextrin and then into glucose.

76. Paper, a form of cellulose, is now made from the fibers of many varieties of plants, and from materials (rags, for example) originally made from vegetable fibers. Almost any form of vegetable matter could, with proper treatment, be reduced to pulp which could be used as a basis for paper.

Wood, straw, and most other vegetable structures are composed of innumerable fibers so small that they can be seen only with the aid of a magnifying glass, and cemented together with other nonfibrous, gummy or resinous materials, usually referred to as *intercellular matter*. The fibers are composed of cellulose, and are of value for forming paper, while the intercellular matter is of no value for forming paper. The aim of all paper-making processes is to wash or dissolve out all intercellular matter, leaving the pure fibers of cellulose in the form of pulp that can be made into paper by mechanical treatment.

Cotton fiber, which is more nearly pure cellulose than any other naturally occurring substance, contains about 90 per cent. of cellulose; linen contains from 70 to 80 per cent., depending on the quality of the flax from which it is made; spruce wood contains from 51 to 56 per cent., depending on the variety and the age of the tree; jute, from 60 to 64 per cent; various straws, from 48 to 63 per cent.; esparto grass, from 46 to 59 per cent.; and manila hemp about 50 per cent.

77. Manufacture of Wood Pulp.—By far the greater quantity of paper used at present is made from wood pulp made by two distinct classes of methods. The first class includes the mechanical process, which results in mechanical wood pulp, or ground wood. The second class includes the various chemical methods, which produce chemical pulp or cellulose. These chemical methods are three in number: the sulphite process, the soda process and the sulphate, or kraft, process.

In the sulphite process, wood chips, properly prepared, are digested with an acid liquor at a high temperature and pressure. The acid liquor is chemically a solution of bisulphite of calcium. It is frequently referred to as *acid*, and the plant for making it in a pulp mill is called the *acid plant*. This liquor has the property of dissolving and removing all the constituents of the wood chips except the cellulose, which, in impure form, constitutes the unbleached sulphite pulp. When bleached with chlorine this pulp is practically pure cellulose. The yield of bleached pulp will vary from 49 to 53 per cent. of the weight of the prepared wood.

The soda process is based on the fact that a caustic-soda solution at high temperatures will dissolve all the other constituents of wood except the cellulose, leaving the latter in a form suitable for paper manufacture.

The sulphate process is a modification of the soda process in which sodium sulphate is used to replace soda ash.

78. Manufacture of Paper.—In making paper from wood pulp, the latter is mixed with sufficient water so that it will flow easily and the mixture is then caused to flow on to the rapidly moving endless screen of the paper machine. The water passes through the screen and the thin layer of partly dried pulp is picked up at the far end of the screen by a series of rolls, being supported at all times by a layer of felt that travels with the rolls. Due to the heat and the pressure of the rolls, the layer of pulp rapidly becomes drier and stronger as it moves forwards and finally becomes sufficiently strong so that the supporting felt is no longer required. It is then passed through polished calender rolls that convert it into finished paper.

79. Amyloid and Vegetable Parchment.—When cellulose is treated with strong sulphuric acid, it dissolves and hydrolyzes. On dilution of the solution obtained in this manner, with water, a jelly-like product called *amyloid* results.

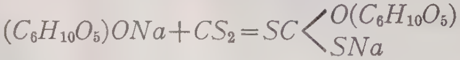
If the cellulose is in the form of a sheet of unsized paper and the latter is immersed for a short time in 80-per-cent. sulphuric acid and then washed and dried, a layer of amyloid will form on the surface of the paper. This treatment renders the paper tough and strong and converts it into a material closely resembling natural parchment. Therefore, as it is derived from cellulose, it is called *vegetable parchment*.

80. Mercerizing.—When cotton thread or fabric is treated with a cold 20-per-cent. solution of sodium hydroxide, the cellulose is converted into a sodium cellulose which, on being washed with water, is converted into a hydrocellulose. The treatment with caustic soda effects a striking change in the physical structure of the cotton fiber and in the appearance of the fabric. Thus, the flat cotton fiber becomes thicker and cylindrical in shape and has the appearance of a silk fiber. Mercerized-cotton cloth looks and feels a great deal like silk and is more easily colored by dyes than is ordinary cotton. In fact, a good many dyes that are used to color mercerized cotton cannot be used successfully to color ordinary cotton.

81. Artificial Silk.—Most of the artificial silk in use today is made by the *viscose process*. In this process wood pulp made by the sulphite process is soaked in a caustic soda solution which mercerizes the fibers and forms sodium cellulose.

$$C_6H_{10}O_5+NaOH=(C_6H_{10}O_5)ONa+H$$

The excess caustic soda is then removed from the sodium cellulose by pressing. The latter is then reduced to shreds and allowed to age in small iron containers at a constant temperature. After aging, the sodium cellulose is placed in rotating drums and treated with carbon bisulphide which is caused to drip slowly into the drum. The reaction that takes place between the sodium cellulose and the carbon disulphide may be represented by the following equation:



$$(C_6H_{10}O_5)ONa+CS_2=SC\begin{cases}O(C_6H_{10}O_5)\\SNa\end{cases}$$

cellulose
xanthate

The course of the reaction is observed by the operator through a sight-glass in the drum. On the introduction of the carbon bisulphide, the sodium cellulose turns from a white to a pale-yellow color, then to a light-orange and finally to an orange. When the orange color is obtained, the rotation of the drum is stopped and its contents discharged into a mixer in which the cellulose xanthate is dissolved in sufficient water to produce an orange-colored solution of high viscosity. The viscosity of this solution is responsible for the name of the process. Before the solution can be used in the making of artificial silk thread, it must undergo a ripening process, which is in many respects similar to the aging process for sodium cellulose. During the ripening process, the cellulose xanthate polymerizes and tends to become less soluble and when judged to be sufficiently ripened, it is ready for spinning. The spinning consists in bringing the viscose solution to the spinning machine under a constant pressure and forcing it through jets or nozzles having openings the diameters of which are about .004 inch. As it leaves the jets the viscose comes in contact with an acid bath and the acid causes the immediate precipitation of the cellulose as such. Each hole in the jet represents a filament of cellulose. These filaments are drawn together to form a thread of artificial silk. The thread is wound on a spool and then washed with water to remove the last trace of acid. When this has been accomplished, the product is dried and may then be handled as is any other textile fiber in the manufacture of a fabric.

82. Nitrocelluloses.—The nitrocelluloses, or, more correctly, the cellulose nitrates, are made by treating cellulose in the form of cotton or paper with a mixture of nitric and sulphuric acids. The degree of nitration obtained depends on the concentration of the acids, the period of nitration and the temperature. Thus, with concentrated nitric acid, a long period of nitration and a comparatively high temperature, a product will be obtained that is more completely nitrated than is the case when a weaker nitric acid is used at a lower temperature and for a shorter period of time. The degree of nitration largely determines the properties of the product. Cellulose nitrates that contain less than about 13 per cent. of nitrogen are called *pyroxylins*. Those that contain over 13 per cent. and up to 13.7 per cent. of nitrogen, which is practically as high as cellulose can be nitrated, are called *guncottons*.

83. Nitration of Cellulose.—The nitration of cellulose is carried out by several processes that vary in the mechanical details. In the dipping process the cellulose is immersed in the mixture of acids for about 10 minutes. It is then removed and placed in acid-proof stone ware pots, the temperatures of which are regulated, and allowed to remain until the desired degree of nitration is obtained. The nitrated cellulose is then transferred to a centrifuge and the excess acid removed. In another process, the cellulose after dipping, is placed directly in the centrifuge in which it remains for the necessary time to effect nitration, and is then freed from excess acid by the operation of the centrifuge. In the displacement process, the cellulose to be nitrated is placed on the false perforated bottom of an acid-proof stoneware tank, having a slightly conical bottom, and then covered with a perforated acid-proof stoneware cover. The mixed acid is then introduced until the cellulose is covered with it. Then a small quantity of water is carefully poured over the acid. Under these conditions the two liquids do not mix and the water prevents the escape of acid fumes. The cellulose is left in contact with the acid for about an hour before the latter is withdrawn by means of a pipe at the bottom of the tank. During the operation of withdrawing the acid, water is let in over the cotton at the same rate as the acid flows out at the bottom. In this manner most of the acid is removed.

84. Purification of Nitrocellulose.—In order that nitrocellulose may be safely stored for use at some future time, it must be thoroughly purified. Purification is accomplished by beating it to a pulp in special apparatus, after which it is repeatedly boiled and washed with fresh water. The product is tested for acidity from time to time during the washing process. The test is made by heating to 65° C. a sample of the nitrocellulose with water in a test tube. A piece of filter paper that has been treated with a potassium-iodide-starch solution is placed in the test tube at the beginning of the heating, and if no iodine is liberated at the end of one hour, which is indicated by the absence of a blue color on the paper, the nitrocellulose is regarded as being acid-free. After removing all but about 15 per cent. of water by pressing, the nitrocellulose is ready to be made up into other products or it may be stored. The water left in greatly decreases the dangers connected with the handling and storage of the material.

85. Guncotton.—Guncotton looks like ordinary cotton, but is rougher to the touch. It is insoluble in alcohol or ether or even in a mixture of the two. A loose tuft of guncotton when ignited burns quietly, leaving no residue, but produces a large volume of gaseous products. It can be caused to explode by the detonation of a small quantity of fulminate of mercury. It is, however, unsuitable for artillery use without modification, owing to its bursting action.

The velocity of its explosion is moderated for artillery use by dissolving the guncotton in acetone or ethyl acetate, which gelatinizes it. After the solvent has been removed, an amorphous substance is left. This has the same chemical composition as guncotton, but burns and explodes more slowly. In this form it is used as a constituent of smokeless powders.

86. Celluloid.—Celluloid is made by nitrating cellulose, in the form of tissue paper, until it contains 10.8 to 11.6 per cent. of nitrogen, and then mixing and kneading the purified nitrocellulose with camphor. The pasty mass obtained in this manner is then heated and pressed in the form of blocks and allowed to cool. The blocks of celluloid thus obtained are worked up into finished celluloid products. If a colored celluloid is desired, the coloring matter is mixed with the nitrocellulose and camphor during the kneading operation.

Celluloid softens on being heated and may be molded by dies to any desired shape It may also be machined, cut, or sawed. It is very inflammable.

87. Dextrin, $C_6H_{10}O_5$.—Dextrin is prepared by moistening starch with nitric acid, allowing it to dry in the air, and then heating it to 110° C. Further treatment with acids converts it into glucose. It is an uncrystallizable solid composed of several isomeric substances resembling each other very closely; it is soluble in water, but is precipitated by alcohol. It is strongly dextrorotatory, and reduces Fehling's solution. It is used as a substitute for gum.

88. Glycogen, $C_6H_{10}O_5$.—Glycogen, a substance closely resembling starch, is found in the livers of animals. It is obtained by exhausting the livers with water, and precipitating the glycogen with boiling alcohol. It is a white or a yellowish-white amorphous powder; it is soluble in water and forms an opalescent solution. It is dextrorotatory, and on hydrolysis the final product is dextrose. It does not reduce Fehling's solution and does not ferment with yeast.

89. Inulin, $C_6H_{10}O_5$.—Inulin occurs in the roots of the dahlia, in chicory, and in other roots. It is obtained from dahlia roots in the form of a colorless, starch-like mass, or white powder, by boiling with water. It swells in cold water, in which it is only slightly soluble, but is readily soluble in boiling water. Continued boiling with water completely changes it into fructose. It turns the plane of polarized light to the left. On hydrolysis it yields fructose.

GLUCOSIDES

90. General Properties.—The glucosides are a class of substances that occur widely distributed in the vegetable kingdom. They have a very high molecular weight, and possess the property of being resolved into a sugar, usually glucose, and some other substance, by the action of dilute acids or by enzymes. While possessing this property in common, in other respects they appear to have no relation to each other. They are mostly all neutral bodies, although they frequently combine with lead oxide and mercuric oxide. They are generally soluble in water and alcohol, very frequently insoluble in ether, and can generally be crystallized. Many glucosides show a levorotatory character, although this rotatory power does not correspond in any way to that of the sugar obtained from the decomposition of the glucoside.

91. Amygdalin, $C_{20}H_{27}NO_{11}$.—Amygdalin occurs in bitter almonds and in the kernels of various fruits such as apples, pears, peaches, and plums. It is extracted principally from almonds. It forms white crystals having a slightly bitter taste, is soluble in water, from which it crystallizes with three molecules of water of crystallization, is only slightly soluble in alcohol, and melts at 200° C. with decomposition. On hydrolysis it breaks down into glucose, benzaldehyde, and hydrocyanic acid:

$$C_{20}H_{27}NO_{11}+2H_2O=2C_6H_{12}O_6+C_6H_5\cdot CHO+HCN$$

The same decomposition is effected by means of the ferment emulsin, which is present in bitter almonds. This ferment is soluble in water and acts only in the presence of water.

92. Æsculin, $C_{15}H_{16}O_9$.—Æsculin occurs in the bark of the horse-chestnut tree. It is a white, crystalline substance with a bitter taste, is soluble in water, alcohol, chloroform, and very soluble in dilute alkalies. Its aqueous solution has a faint blue fluorescence. It melts at 160° C. with decomposition. Dilute acids or ferments decompose it into glucose and æsculetin:

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4$$

93. Salicin, $C_{13}H_{18}O_7$.—Salicin is obtained from the leaves of willow and poplar trees. It forms lustrous, white needles of an exceedingly bitter taste which melt at 200° C., with decomposition. It burns with a bright flame, leaving a residue of carbon. Salicin is insoluble in ether, soluble in twenty-one parts of cold water, in four parts of hot water, and is more soluble in alcohol. It gives a bright-red color with sulphuric acid. Emulsin resolves salicin into glucose and salicylic alcohol:

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_7H_8O_2$$

94. Populin, $C_{20}H_{22}O_8$.—Populin is obtained from the bark and leaves of the aspen. Populin crystallizes in fine, silky, colorless needles having two molecules of water of crystallization. It has a sweetish taste somewhat resembling licorice. It is soluble in hot alcohol, acetic acid, and dilute mineral acids, but is only very slightly soluble in water. It melts at 180° C. It really appears to be benzoyl salicin, as is shown by hydrolysis, which splits populin into benzoic acid and salicylic alcohol.

95. Phloridzin, $C_{21}H_{24}O_{10}$.—Phloridzin exists in the roots and bark of apple, pear, plum, and cherry trees. It is extracted by boiling the roots with water, concentrating the solution, and allowing it to stand in a cool place. Phloridzin crystallizes from this solution in small white, silky needles having a sweet taste with a bitter after taste. It is soluble in alcohol and hot water, and melts at 108° C. It then solidifies and again melts at 170° C. By hydrolysis it is decomposed into glucose and phloretin, according to the equation

$$C_{21}H_{24}O_{10} + H_2O = C_{15}H_{14}O_5 + C_6H_{12}O_6$$

96. Coniferin, $C_{16}H_{22}O_8$.—Coniferin is an important glucoside that occurs in the coniferæ. By hydrolysis or under the action of emulsin it is decomposed into glucose and coniferyl alcohol, according to the equation

$$C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3$$

MIXED COMPOUNDS CONTAINING NITROGEN

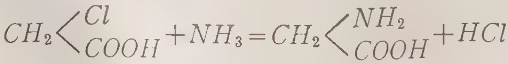
AMINO ACIDS

97. Introductory.—The principal mixed compounds containing nitrogen are the amino acids and the acid amides. They are of importance because many of them are the products of decomposition of proteins, and because they represent favorite forms of combination in nature. Many of these substances are found in the animal kingdom, and many of the most important are found in the animal body.

98. Structure.—The relation of the amino acids to the simple acids is the same as the relation of the amino derivatives of the hydrocarbons is to the hydrocarbons. In other words, the amino acids may be regarded as acids in which an atom of hydrogen has been replaced by the amino group NH_2. Thus, as methyl amine, or amino methane, has the formula $CH_3{\cdot}NH_2$, aminoacetic acid has the formula $CH_2{\cdot}NH_2{\cdot}COOH$.

99. General Properties.—As the amino acids contain both the basic NH_2 group and the acidic $COOH$ group, they form salts with both bases and acids. By replacing the hydrogen of the amino group by radicals, amino acids of a more complicated character are obtained. The amino acids behave in most respects like the amines. With nitrous acid they yield hydroxy acids, just as the amines yield alcohols.

100. Preparation.—The amino acids may be prepared by the action of ammonia on the halogen substituted acid, as is shown by the equation



$$CH_2{<}\begin{array}{l}Cl\\COOH\end{array}+NH_3=CH_2{<}\begin{array}{l}NH_2\\COOH\end{array}+HCl$$

chlor acetic acid amino acetic acid

They may also be obtained by treating the aldehydes and ketones with hydrocyanic acid, forming a hydroxy nitrile, which, on treatment with ammonia and hydrolization of the nitrile of the amino acid formed, gives the amino acid. Thus,

$$CH_3CHO + HCN = CH_3CHOH\cdot CN$$

acetaldehyde — Nitrile of alpha-hydroxy propionic acid

$$CH_3CHOH\cdot CN + NH_3 = CH_3CH\cdot NH_2\cdot CN + H_2O$$

Nitrile of alpha-amino propionic acid

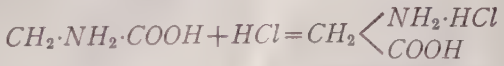
$$CH_3CH\cdot NH_2\cdot CN + 2H_2O = CH_3CH\cdot NH_2\cdot COOH + NH_3$$

alpha-amino propionic acid

101. Amino Acetic Acid, $CH_2\cdot NH_2\cdot COOH$.—Amino acetic acid, also known as *glycocoll* and *glycine*, can be obtained by boiling glue with dilute sulphuric acid. It derives the name glycocoll from this method of formation and from its sweet taste.

Amino acetic acid crystallizes from its aqueous solution in large rhombic prisms that are soluble in four parts of cold water, but are insoluble in absolute alcohol or in ether. It melts at 232° C., with decomposition. Ferric chloride imparts an intense red color to ammoniacal solutions of amino acetic acid. This color is discharged by acids.

As amino acetic acid has both acid and basic properties, it unites with acids to form weak salts and with bases to give salts with metals. Thus,



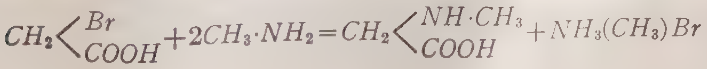
$$CH_2\cdot NH_2\cdot COOH + HCl = CH_2\left<\begin{array}{l}NH_2\cdot HCl\\ COOH\end{array}\right.$$

amino acetic acid hydrochloride

$$CH_2\cdot NH_2\cdot COOH + NaOH = CH_2\cdot NH_2\cdot COONa + H_2O$$

sodium amino acetate

102. Methyl Amino Acetic Acid, $CH_2\cdot NH\cdot CH_3\cdot COOH$. Methyl amino acetic acid or as it is also called, *sarcosine*, or methyl glycocoll, was first obtained by Liebig as a decomposition product of the creatine contained in beef extract. It is prepared by treating bromacetic acid with methyl amine; thus,



$$CH_2\left<\begin{array}{l}Br\\ COOH\end{array}\right. + 2CH_3\cdot NH_2 = CH_2\left<\begin{array}{l}NH\cdot CH_3\\ COOH\end{array}\right. + NH_3(CH_3)Br$$

Sarcosine is also a decomposition product of caffeine, a constituent of tea and coffee. It is a deliquescent, transparent, crystalline solid with a sweetish taste. It melts at 215° C., is slightly soluble in alcohol, and readily soluble in water.

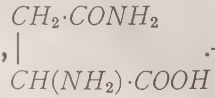
103. Leucine, $C_5H_{10}\cdot NH_2\cdot COOH$.—Leucine was discovered in old cheese by Proust in 1818. It is found widely distributed in the glands of animals and human beings, and in the sprouts of plants. It is formed by the decomposition of albumins and gelatins, and when horn, gelatinous tissues, or albuminous bodies are boiled with sulphuric acid, or fused with caustic potash. It is *α-amino-caproic acid*, although it is probable that there are several leucines. The artificially prepared α-amino-caproic acid appears to be identical with the leucine obtained from casein. That, however, obtained from vegetable albumin and from glue and horn is α-amino-isobutyl-acetic acid.

Leucine prepared from casein, crystallizes in pearly scales that have a fatty feeling, melts at 270° C., and, when carefully heated, sublimes without decomposition. It is soluble in water and alcohol, and is neutral in its reactions, forms compounds with both acids and bases, and has the formula $CH_3\cdot(CH_2)_3\cdot CH(NH_2)\cdot COOH$. Hydriodic acid converts it into caproic acid and ammonia; thus,

$$C_5H_{10}NH_2\cdot COOH+2HI=C_5H_{11}\cdot COOH+NH_3+I_2$$

Nitrous acid converts leucine into hydroxy caproic acid; thus,

$$C_5H_{10}NH_2\cdot COOH+HNO_2=C_5H_{10}(OH)\cdot COOH+H_2O+N_2$$

104. Asparagine,  $\begin{array}{l}CH_2\cdot CONH_2\\ |\\ CH(NH_2)\cdot COOH\end{array}$.—Asparagine is a derivative of aspartic or amino succinic acid, which, in turn, is derived from succinic acid, $(CH_2)_2(COOH)_2$ by the replacement of one hydrogen atom of a CH_2 group with an amino group. Asparagine occurs naturally in many plants such as asparagus, peas, beans, beets, vetches, licorice wood, wheat, and the roots of the marshmallow. It can be prepared from marshmallow roots by macerating the chopped roots in the cold with milk of lime, precipitating the filtered liquid with barium carbonate, and evaporating the clear solution. It can also be prepared by treating monoethyl amino succinate with ammonia.

Asparagine crystallizes in large, transparent, lustrous, rhombic prisms, that have a specific gravity of 1.52 and a faint cooling taste. They are moderately soluble in hot water, but are insoluble in alcohol and ether. Asparagine acts as a weak acid and also a weak base. Ferments convert it into ammonium succinate, and boiling with acids or alkalies causes it to break up into aspartic acid and ammonia. Nitrous acid converts asparagine into malic acid.

ACID AMIDES

105. Methods of Preparation.—Acid amides may be prepared by three general methods:

1. By heating the ammonium salt of the acid. The salt splits up into the acid amide and water.

$$CH_3{\cdot}COONH_4 = \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

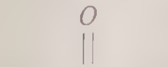
2. Treatment of an ethereal salt of an acid with ammonia; thus,

$$CH_3{\cdot}COOC_2H_5 + NH_3 = CH_3{\cdot}CONH_2 + C_2H_5{\cdot}OH$$

3. Treatment of an acid chloride with ammonia; thus,

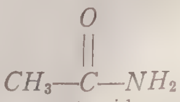
$$CH_3{\cdot}COCl + 2NH_3 = CH_3{\cdot}CONH_2 + NH_4Cl$$

106. Acetamide, $CH_3{\cdot}CONH_2$.—Acetamide may be formed by any of the reactions given, but the reaction between acetyl chloride and ammonia best shows the relation existing between the acid and the amide. Thus, acetamide is acetic acid in which hydroxyl has been replaced by the amino group. This relation is clearly shown by the formulas



$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH$$

acetic acid

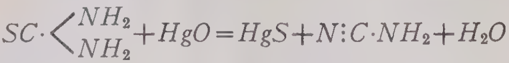


$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}NH_2$$

acetamide

Acetamide is a hygroscopic, crystalline, solid soluble in water, alcohol and ether. The crystals melt at 82° C., to a liquid that boils at 222° C.

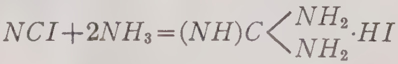
107. Cyanamide, $N{:}C\cdot NH_2$.—Cyanamide is formed by the action of cyanogen chloride or bromide on ammonia in ethereal solution and also when the oxides of mercury or silver react with sulpho-urea, $SC\cdot(NH_2)_2$. The latter reaction is shown by the equation,



$$SC\cdot\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}+HgO=HgS+N{:}C\cdot NH_2+H_2O$$

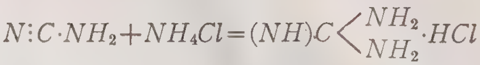
It is a crystalline solid that melts at about 43° C. and is soluble in alcohol and water. Like the other simple compounds of cyanogen, this compound readily undergoes change. When undisturbed it changes into *dicyandiamide*, $C_2N_4H_4$, and when heated to 150° C. a violent reaction occurs with the formation of *tricyantriamide*, $C_3N_6H_6$.

108. Guanidine, CN_3H_5.—Guanidine is closely related to cyanamide. It was first obtained by the oxidation of guanine, found in guano, with hydrochloric acid and potassium chlorate. It is also prepared by treating cyanogen iodide with ammonia, as is shown by the reaction



$$NCI+2NH_3=(NH)C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}\cdot HI$$

Guanidine may also be prepared by treating an alcoholic solution of cyanamide with ammonium chloride at 100° C.; thus,



$$N{:}C\cdot NH_2+NH_4Cl=(NH)C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}\cdot HCl$$

Guanidine is a strongly alkaline base that forms deliquescent, crystalline salts with acids. Boiled with dilute sulphuric acid, it is converted into urea with the evolution of ammonia; thus,

$$CN_3H_5+H_2O=\underset{\text{urea}}{CON_2H_4}+NH_3$$

109. General Properties.—Since in the preparation of the acid amides the acid hydrogen of the acid has been replaced by the amino group, and as the basic properties of the ammonia are overcome by the presence of the acid radical, the amides are neutral.

Boiling with strong bases converts the acid amides into ammonia and the salt of the acid; for instance,

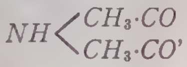
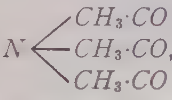
$$CH_3{\cdot}CONH_2+KOH=NH_3+CH_3{\cdot}COOK$$

Phosphorus pentoxide converts the acid amides into cyanides; thus,

$$CH_3{\cdot}CONH_2=CH_3CN+H_2O$$

As the amide can be made from the ammonium salt and the cyanide from the amide, the amide and the ammonium salt can be made from the cyanide; thus,

$$R{\cdot}COONH_4 \rightarrow R{\cdot}CONH_2 \rightarrow R{\cdot}CN$$
$$R{\cdot}CN \rightarrow R{\cdot}CONH_2 \rightarrow R{\cdot}COONH_4$$

By treating acid amides with strong acids more complicated compounds, such as *diacetamide*,  $NH\begin{cases}CH_3{\cdot}CO\\CH_3{\cdot}CO\end{cases}$, and *triacetamide*,  $N\begin{cases}CH_3{\cdot}CO\\CH_3{\cdot}CO\\CH_3{\cdot}CO\end{cases}$, may be obtained.

If an amide of a polybasic acid is boiled with ammonia, a partial decomposition takes place and a substance that is both an amide and an acid is obtained. Thus, when *oxamide* is so treated, *oxamic acid* is formed; or,

$$(CONH_2)_2 \rightarrow CONH_2{\cdot}COOH$$

TABLE II

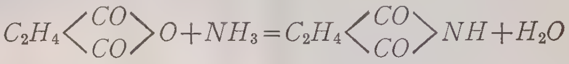
ACID AMIDES OF FATTY-ACID SERIES

Name	Symbol	Melting Point Degrees C.	Boiling Point Degrees C.
Formamide	$HCO{\cdot}NH_2$		212
Acetamide	$CH_3CO{\cdot}NH_2$	83	223
Glycolamide	$CH_2(OH)CO{\cdot}NH_2$	120	
Lactamide	$C_2H_4(OH)CO{\cdot}NH_2$	74	
Oxamide	$(CONH_2)_2$	Decomposes at 200	
Succinamide	$C_2H_4(CONH_2)_2$	243	

110. Table II gives the properties of some of the more common acid amides of the fatty-acid series.

ACID IMIDES

111. Succinimide, $C_2H_4 \cdot (CO)_2 \cdot NH$, belongs to a class of compounds known as *acid imides*. They may be regarded as anhydrides in which an oxygen atom has been replaced by the imino group NH. They are also formed from the amides by the loss of ammonia. Succinimide is formed by heating succinic anhydride is a current of ammonia; thus,



$$C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O+NH_3=C_2H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}NH+H_2O$$

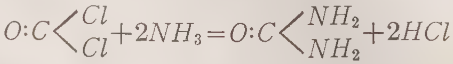
It forms colorless rhombic plates that melt at 126° C. and boil at 280° C. It is readily soluble in both water and alcohol, has weak acid properties, and forms salts with the metals.

UREA AND DERIVATIVES

112. Urea, $O:C(NH_2)_2$.—Urea, or *carbamide*, may be regarded as the diamide of carbonic acid. Its importance and certain peculiarities warrant its being treated by itself. It was discovered in urine by Von Rouelle in 1773, and was synthesized by Wöhler, who obtained it by heating an aqueous solution of ammonium isocyanate. Urea was the first organic compound prepared synthetically.

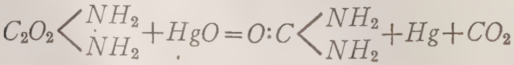
Urea is found in the urine and blood of all mammals. The human adult voids, on an average, about 30 grams of urea daily. It is most readily obtained from urine, but is made by the following methods:

1. By the action of ammonia on carbonyl chloride; thus,



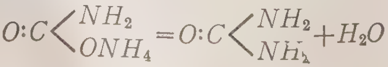
$$O:C{<}\begin{matrix}Cl\\Cl\end{matrix}+2NH_3=O:C{<}\begin{matrix}NH_2\\NH_2\end{matrix}+2HCl$$

2. By heating oxamide with mercuric oxide; thus,



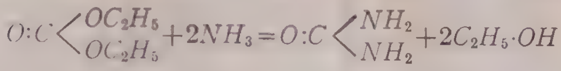
$$C_2O_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}+HgO=O:C{<}\begin{matrix}NH_2\\NH_2\end{matrix}+Hg+CO_2$$

3. By heating ammonium carbamate; thus,



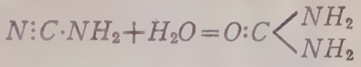
$$O:C{<}\begin{matrix}NH_2\\ONH_4\end{matrix}=O:C{<}\begin{matrix}NH_2\\NH_2\end{matrix}+H_2O$$

4. By the action of ammonia on ethyl carbonate; thus,



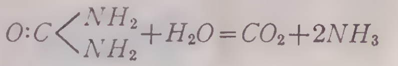
$$O{:}C\Big\langle\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}+2NH_3=O{:}C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}+2C_2H_5{\cdot}OH$$

5. By adding water to cyanamide; thus,



$$N{:}C{\cdot}NH_2+H_2O=O{:}C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}$$

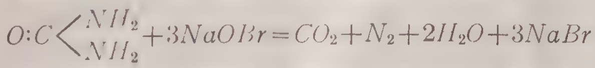
113. Properties.—Urea crystallizes from alcohol in long rhombic prisms that have a cooling taste. It melts at 132° C., is soluble in cold water and in alcohol, but is almost insoluble in ether. When urea is heated with water to 100° C. or when boiled with alkalies or acids, it decomposes into carbon dioxide and ammonia; thus,



$$O{:}C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}+H_2O=CO_2+2NH_3$$

After urea has left the body, it ceases to be of value. On exposure to the atmosphere, however, its decomposition results because of the action of an organism, carbon dioxide, and ammonia being formed as in the reaction just given. In this way nature converts a waste product into a useful material.

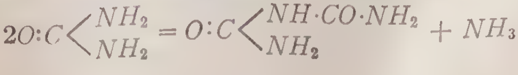
An alkaline hypobromite decomposes urea into nitrogen, carbon dioxide, and water, as is shown by the equation



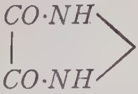
$$O{:}C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}+3NaOBr=CO_2+N_2+2H_2O+3NaBr$$

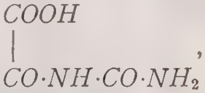
This reaction is the basis of one of the methods used to estimate the urea in urine. The carbon dioxide is absorbed by a solution of caustic potash and the nitrogen is measured.

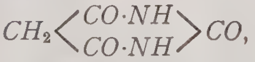
Urea unites with acids, bases, and salts, and the hydrogen of the amino groups can be replaced by acid or alcohol radicals yielding compounds such as *ethyl urea*, $O{:}C\Big\langle\begin{matrix}NH{\cdot}C_2H_5\\NH_2\end{matrix}$, and *acetyl urea*, $O{:}C\Big\langle\begin{matrix}NH{\cdot}CO{\cdot}CH_3\\NH_2\end{matrix}$. When heated above 150° C. urea loses ammonia and forms *biuret* or *allophanamide;* thus,

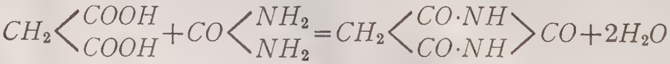


$$2O{:}C\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}=O{:}C\Big\langle\begin{matrix}NH{\cdot}CO{\cdot}NH_2\\NH_2\end{matrix}+NH_3$$

114. Ureids.—Ureids are the result of the substitution of acid residues for one or more of the hydrogen atoms of urea. The relation between the acid and urea in the ureid is like that between the acid and ammonia in the amide. The ureids of the dibasic acids resemble in the same way the amides of these acids. Thus *oxalyl urea,*  $\left.\begin{matrix}CO\cdot NH\\ |\\ CO\cdot NH\end{matrix}\right>CO$, is formed by boiling uric acid with strong nitric acid or other oxidizing agents, and by treating a mixture of oxalic acid and urea with phosphorus oxychloride. It has acid properties, forming salts with the metals. These salts, when treated with water, readily pass over into salts of oxaluric acid.

Oxaluric acid,  $\begin{matrix}COOH\\ |\\ CO\cdot NH\cdot CO\cdot NH_2\end{matrix}$, bears the same relation to oxalyl urea as oxamic acid bears to oxamide. It occurs in human urine as the ammonium salt. Phosphorus oxychloride converts it into oxalyl urea.

Barbituric acid,  $CH_2\left<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}\right>CO$, or *malonyl urea,* is, like oxalyl urea, obtained from uric acid. It is prepared by treating a mixture of malonic acid and urea with the oxychloride of phosphorus. This reaction is shown by the equation



$$CH_2\left<\begin{matrix}COOH\\ COOH\end{matrix}\right.+CO\left<\begin{matrix}NH_2\\ NH_2\end{matrix}\right.=CH_2\left<\begin{matrix}CO\cdot NH\\ CO\cdot NH\end{matrix}\right>CO+2H_2O$$

Alkalies decompose barbituric acid into malonic acid and urea.

URIC ACID

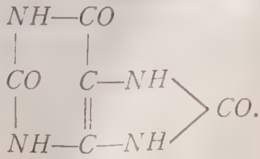
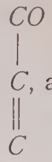
115. Occurrence and Preparation.—Uric acid, $C_5H_4N_4O_3$, occurs in small quantities in human urine, in the urine of carnivorous animals, and in the excrement of birds and reptiles. Human urine yields uric acid in the form of small crystals, when it is concentrated by evaporation or is mixed hot with hydrochloric or nitric acid. Guano, the partly decomposed excrement of sea birds, contains a considerable quantity of uric acid; this may be extracted by boiling with borax, and adding hydrochloric acid to the solution. In gout, uric acid is deposited in the joints, under the skin, and in the bladder, in the form of insoluble acid salts. It is prepared synthetically by heating a mixture of urea and glycine to about 230° C. This reaction is represented by the equation

$$3O{:}C(NH_2)_2+NH_2CH_2COOH=C_5H_4N_4O_3+3NH_3+2H_2O$$

116. Properties.—Uric acid forms white crystalline scales that are soluble in hot sulphuric acid, very slightly soluble in water, and insoluble in alcohol and ether. It decomposes on heating without fusing. It is odorless and tasteless, and acts like a weak dibasic acid. When carbon dioxide is led into a solution of a neutral urate, a nearly insoluble acid urate is precipitated. Hydrochloric acid added to a urate forms a thick, white, gelatinous precipitate of uric acid. Heated to 160° C., with an excess of hydriodic acid, uric acid is decomposed into carbon dioxide, glycine, and ammonia, as is shown by the equation

$$C_5H_4N_4O_3+5H_2O=NH_2CH_2COOH+3CO_2+3NH_3$$

A general test for uric acid, and one which permits the detection of the smallest trace of it, is the formation of the substance known as *murexide*. This substance is formed by treating uric acid with nitric acid, and slowly evaporating the solution. A residue is left that assumes a purple color on the addition of a drop of ammonia.

117. Structure.—When the lead salt of uric acid is treated with methyl iodide, two isomeric methyl uric acids are formed. These can be converted into a tetramethyl uric acid, which is derived from uric acid by the substitution of four methyl groups for the four hydrogen atoms of uric acid. This acid decomposes, giving off the methyl groups in combination with nitrogen as methyl amine. This and other transformations show that uric acid has the constitution  . According to this formula, uric acid contains two residues of urea combined in different ways with the group  $\overset{\overset{CO}{|}}{\underset{\underset{C}{\|}}{C}}$, and may be regarded as a diureid of a trihydroxyacrylic acid. The artificial preparation of uric acid confirms the correctness of this view.

PROTEINS

INTRODUCTORY

118. Occurrence.—Those substances that are known as *proteins* are found in every living cell and consequently are of great importance. The common sources of proteins are the whites of eggs, the gluten of wheat and the casein of milk.

119. Composition.—The compositions of the different kinds of proteins do not vary to any great extent. They all contain carbon, hydrogen, oxygen, nitrogen, and sulphur, within the following limits:

	PER CENT.
Carbon	50.0 to 55.0
Hydrogen	6.5 to 7.3
Oxygen	19.0 to 24.0
Nitrogen	15.0 to 18.0
Sulphur	.4 to 2.4

A few proteids containing phosphorus, the phosphoproteids, are known.

It is worthy of note that the average nitrogen content of the proteins is about 16 per cent., as this fact forms the basis of the method used in the estimation of the protein content of a substance. Thus, since $100 \div 16 = 6.25$, it is merely necessary to determine the nitrogen content of the substance containing the protein and then multiply it by 6.25 in order to obtain the protein content.

120. Structure.—Very little is known concerning the structure of the proteins, and their investigation is hindered, for the reason that methods at the disposal of chemists cannot be applied because of their properties. Thus, they do not crystallize and they cannot be distilled without decomposition. It is very probable, however, that the proteins are compounds of very high molecular weight. Thus, based on the per cent. of sulphur present, the molecular weight of egg albumin is estimated to be about 15,000.

121. General Properties.—As already stated, the proteins do not crystallize, nor can they be distilled without decomposition. On being heated to about 50 to 75°C., they coagulate. In some cases, coagulation is also caused by acids or alcohol. Proteins are insoluble in alcohol and ether and only a few dissolve in water. Most of them, however, will dissolve in salt solutions. Proteins are colloidal in nature, and this property is taken advantage of in separating them from salts and crystalloids.

The proteins act like weak acids, in that compounds insoluble in water result on the addition of salts of most of the heavy metals. Some weak acids also yield insoluble compounds, showing that the proteins also act like bases. The proteins are completely precipitated from their solutions by phosphotungstic acid. This method, in addition to coagulation by boiling and precipitation by alcohol, is used to separate the proteins from solution.

Very dilute hydrochloric acid causes most albuminoids to swell up and be converted into a transparent jelly partly soluble in water, whereas concentrated hydrochloric acid dissolves them, the acid assuming a dark-blue to violet color. Nitric acid colors albuminoid matter yellow. When the proteins are boiled with dilute acids, amino acids are obtained.

122. Albumin.—Albumin, or white of egg, can be extracted from the aqueous solution in the egg by breaking up the membrane, neutralizing the solution, filtering, dialyzing, and removing the fatty matters. The albumin thus obtained is a white or a yellowish-white amorphous solid having a specific gravity of 1.31. In cold water it becomes soft and dissolves like gum. When this solution is heated to 70° C., the albumin is rendered insoluble and coagulates. This coagulated albumin is not readily dissolved in acids or alkalies. Heated with water in a sealed tube to 150° C. it dissolves to a reddish liquid that behaves like a solution of ordinary albumin, but which is not coagulated by heat.

123. Globulin and Fibrin.—The coagulable albuminoid globulin is obtained from the red corpuscles of the blood. It resembles albumin to a large extent, but can be coalgulated completely only by heating to 90° C. Acetic acid and alkalies do not precipitate it; it is thrown down by carbon dioxide. Fresh blood, on standing, soon coagulates and separates into a yellow liquid and a clot. The clot contains the red corpuscles, surrounded by an insoluble albuminoid matter, which is fibrin. This is formed by the reaction of the two globulins fibrinogen and serum globulin, which exist in solution in the liquid portion of the blood.

Fibrin putrefies rapidly at ordinary temperatures, and is converted into a mixture of albumin, leucine, butyric acid, and valeric acid. Hydrochloric acid dissolves fibrin, forming a blue solution. Dilute hydrochloric acid causes fibrin to swell, then to become a transparent jelly, and finally to dissolve in the liquid. Dilute sodium chloride dissolves fibrin. When dialyzed, a limpid solution of the two globulins remains in the dialyzer. This is coagulable by heat and presents many of the properties of egg albumin.

124. Peptones.—When coagulated albumin is digested at about 37° C. with the gastric juice it is peptonized, or converted into peptone. The albumin in the resulting solution is neither coagulated by heat nor precipitated by ammonium sulphate. The constituent of the gastric juice producing this change is pepsin, which can be precipitated from the gastric juice by alcohol. Pepsin resembles albumin in composition. Dilute hydrochloric acid dissolves it, yielding a solution that will peptonize most albumins. The pepsin obtained from the stomachs of many animals is used to aid digestion.

125. Hemoglobin and Oxyhemoglobin.—In its composition, oxyhemoglobin closely resembles albumin, except that it contains some iron and less sulphur. The coloring matter contained in the red globules of the arterial blood is oxyhemoglobin. It is usually obtained from the blood of human beings and some animals, either in the form of a powder or in lustrous scales. These crystals contain oxygen loosely combined, and evolve it when warmed in a vacuum, becoming hemoglobin. On exposure to the air, this again absorbs oxygen, the change being attended with the production of a much brighter red color, and with a difference in its action on transmitted light. Oxyhemoglobin shows the green portion of the spectrum crossed by two black bands, whereas hemoglobin exhibits only one band in the middle of the green. Oxyhemoglobin shaken with carbon monoxide loses its oxygen, absorbs an equal volume of carbon monoxide, and changes to a purple color. Heated above 70° C., oxyhemoglobin decomposes into albumin, which coagulates, and another red coloring matter known as *hematin.*

126. Hematin.—Hematin is formed by the decomposition of oxyhemoglobin. The hydrochloride of hematin forms flat, rhombic prisms of a dark violet-red color and a metallic luster. The formation of these crystals has been employed to identify blood stains. The suspected matter is placed on a microscopic slide, sodium chloride is added, and glacial acetic acid is allowed to run under the cover glass. On heating until bubbles appear, and cooling, the dark-red hematin hydrochloride crystals appear.

127. Casein.—Casein is precipitated from milk by the addition of an acid. The lactic acid formed by the fermentation of milk sugar will have this effect, and the milk is said to *curdle.* It is a white to yellowish-white pwoder and dissolves in alkalies. Fresh milk is alkaline, hence the casein is in the fresh milk in solution. A characteristic property of casein is its coagulation by rennet, the mucous membrane of the stomach of the calf, a small quantity of which coagulates a large quantity of milk. This coagulation does not depend on the formation of lactic acid, but on the specific action of the rennet. The precipitation of casein occurs more readily with acids and rennet when the milk is warmed, but if fresh milk is heated to boiling the decomposition will be prevented.

Legumin, or vegetable casein, is obtained from peas, beans, and most leguminous seeds. It closely resembles casein in its properties, but contains more nitrogen and less sulphur than casein.

128. Gelatine.—When the calcium carbonate and phosphate contained in bones are dissolved out with hydrochloric acid, the cartilaginous substance remains in a semitransparent, elastic mass that retains the form of the bone. This substance, although insoluble in cold water, dissolves on prolonged boiling or by digesting with water heated above 100° C. to a clear solution that sets into a transparent jelly on cooling. It does not form well-defined compounds with other bodies and cannot be vaporized. Its composition approximates the empirical formula $C_{42}H_{66}N_{13}O_{16}$. The name *gelatine* has been given to it because of its behavior with water. It swells and dissolves slightly in cold water, and dissolves readily in hot water, the hot solution forming a jelly when cool. The cellular tissue and the skin scales, and swimming bladders of fish can also be converted into gelatine.

Dry gelatine occurs in semitransparent sheets from yellowish white to dark brown in color, depending on their purity and thickness. Gelatine is precipitated from its aqueous solutions by alcohol and by tannic acid, but by no other acid. Platinic chloride and mercuric chloride precipitate gelatine, but alum and the salts of lead, copper, silver, etc. do not. Dilute sulphuric acid, when boiled with gelatine, converts it into leucine and glycine.

TESTS FOR PROTEINS

129. Millon's Test.—When a few drops of Millon's reagent are added to a protein and the mixture warmed, the color will change from white to red. Millon's reagent is made by dissolving 1 part of mercury in 2 parts of concentrated nitric acid, and then diluting the solution with twice its volume of water. The finished solution contains mercurous nitrate, mercurous nitrite, and nitric acid.

130. Biuret Reaction.—The biuret reaction depends on the formation of a fine red to violet coloration by adding caustic soda to a proteid and then, drop by drop, a 2-per-cent. solution of copper sulphate. Biuret also responds to this test and thus gives it its name.

131. Xanthoprotein Reaction.—The xanthoprotein reaction consists in the formation of a yellow color on treatment of the protein with concentrated nitric acid. This color changes to an orange shade on the addition of ammonia. Care must be taken in interpreting the results of this test, as all compounds that contain the C_6H_5 group respond to it.

ORGANIC CHEMISTRY

(PART 5)

AROMATIC OR BENZENE SERIES OF HYDROCARBONS

SOURCES OF AROMATIC HYDROCARBONS

1. Introductory.—In importance and in the number of members the *aromatic series of hydrocarbons* outranks the paraffin series. The fundamental substance of the aromatic hydrocarbons is *benzene*, C_6H_6. The general formula of the series is C_nH_{2n-6}, in which n is any whole number not less than six. The aromatic hydrocarbons differ in various respects from the aliphatic hydrocarbons, their principal distinction being their greater carbon content. The description of the members of the aromatic series is greatly simplified by the fact that in it the properties of the aliphatic alcohols, aldehydes, acids, etc. are again met with.

2. Original Sources of Aromatic Hydrocarbons.—The earliest known aromatic hydrocarbons were first derived from aromatic oils, such as the oils of lemon, wintergreen, peppermint, bitter almonds, etc., and this source has given name to the series. At the present time practically all hydrocarbons of the aromatic or benzene series are derived from coal tar.

3. Production of Coal Tar.—Coal tar, a thick, black liquid with a characteristic odor, is one of the products obtained when coal is subjected to destructive distillation. Coal, however, is not destructively distilled on a large scale for the sole

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

purpose of producing tar. Therefore, the latter is regarded as a by-product obtained in the manufacture of coke or gas that is to be used for illuminating or industrial purposes.

When coal is heated to redness in retorts from which air is excluded, gaseous and solid products are obtained. The gases are passed through condensers in which the liquid and volatile solid particles are precipitated and recovered as coal tar. The gases that do not condense at the temperature of the condenser go to form, after further purification, what is known as illuminating gas or fuel gas. The solid residue left behind in the retort is coke. The tar, which is of greatest importance to the organic chemist, contains all of the hydrocarbons of the aromatic series that will be treated in this Section, as well as some of the derivatives of these hydrocarbons.

4. Distillation of Coal Tar.—In order to obtain the aromatic hydrocarbons, coal tar is distilled fractionally from iron retorts. The points at which the fractions are collected vary in different countries and also depend on the quality of the tar that is distilled. In Table I are shown the fractions commonly taken.

TABLE I

FRACTIONAL DISTILLATION OF COAL TAR

Name of Product	Temperature of Distillation Degrees C.
Crude naphtha or light oils	Up to 170
Carbolic oil or middle oil	170 to 230
Creosote oils, dead oils, or heavy oils	230 to 270
Anthracene oils	Above 270
Pitch	Residue

5. Treatment of Distillates.—The first fraction collected is called light oil because it will float on water. It contains the principal hydrocarbons of the aromatic series, namely, benzene, toluene, and xylene, together with phenols, some naphthalene, resins, pyridines, and unsaturated compounds.

This portion of the distillate is treated with sulphuric acid to remove the resins, unsaturated compounds, and pyridines. It is then agitated with a solution of caustic soda, which dissolves the phenols, and after being well washed with water it is redistilled.

In the redistillation a fraction is taken, between 80° and 110° C., that consists largely of two important hydrocarbons, *benzene* and *toluene*, and because 90 per cent. of it distills below 100° C., it is called *90 per cent. benzol*. Actually it contains about 70 per cent. of benzene. A second fraction, collected between 110° and 140° C., contains smaller quantities of benzene and toluene together with some *xylene*. This product appears on the market as *50 per cent. benzol* and contains about 45 per cent. of benzene. The third fraction is collected between 140° and 170° C., and contains a large percentage of xylene and some *mesitylene*. It is called *solvent naphtha*.

6. After the temperature has been run up to 170° C., the residue in the still consists largely of phenols and naphthalene and is therefore combined with the second fraction, or carbolic oils, obtained between 170° and 230° C., from the tar itself. This fraction on cooling deposits crystals of naphthalene that are filtered off from the remaining carbolic oil. The crude naphthalene is then treated with sulphuric acid and caustic soda solution as a step in its purification, which is completed by distilling or subliming the crude material.

The carbolic oil is treated with caustic soda solution, which dissolves the phenol. The solution thus formed is separated from the oil that remains and is neutralized with sulphuric acid. The phenol is set free, and after being washed with water is distilled. The distillate is collected in two fractions, one of which crystallizes and consists of very pure phenol. The other fraction does not crystallize and consists of impure phenol.

7. The third fraction of coal-tar distillate, collected between 230° and 270° C., is a green, fluorescent oil. It consists principally of phenols, cresols, naphthalene, and anthracene. It is sold as creosote oil and is extensively used in the preservation of timber.

8. The fourth fraction, collected at 270° C. and above, contains anthracene and other hydrocarbons that are solid at ordinary temperatures. The crystalline hydrocarbons that are obtained when the oil cools are separated from the liquid portion by pressing. The crystals are washed with solvent naphtha, which dissolves out the other hydrocarbons present more readily than it does anthracene. The product obtained in this manner contains a high percentage of anthracene and is used in the manufacture of certain dyes.

The pitch that remains in the still after the anthracene fraction has been collected is used in the preparation of paints, roofing paper, and asphalt.

IMPORTANT MEMBERS OF AROMATIC SERIES

GENERAL PROPERTIES

9. The names of six members of the homologous series of aromatic hydrocarbons, together with their empirical formulas and some of their physical properties, are given in Table II.

TABLE II

IMPORTANT AROMATIC HYDROCARBONS

Name	Formula	Boiling Point Degrees C.	Specific Gravity
Benzene	C_6H_6	80.4	.8784 at 20° C.
Toluene	C_7H_8	110.7	.8613 at 25° C.
Xylene	C_8H_{10}	139.3	.8658 at 20° C.
Mesitylene	C_9H_{12}	164.8	.8634 at 20° C.
Cymene	$C_{10}H_{14}$	176.5	.8551 at 20° C.
Hexamethyl benzene	$C_{12}H_{18}$	264.0	

It will be noted that the difference in composition between successive members of the series, as indicated by the empirical formulas of the hydrocarbons, is equivalent to CH_2, as is the case with successive members of the methane series of hydrocarbons.

BENZENE, C_6H_6

10. Preparation.—As previously stated, benzene is recovered by distillation from the light oil obtained from coal tar. It may also be prepared by heating benzoic acid, C_6H_5COOH, with lime. Thus,

$$C_6H_5COOH+CaO=C_6H_6+CaCO_3$$

Benzene is also formed when acetylene is passed through a tube heated to about 600° C. The reaction that takes place is one of polymerization, three molecules of acetylene combining to form one molecule of benzene. Thus,

$$3C_2H_2+\text{heat}=C_6H_6$$

11. Physical Properties.—Benzene is a colorless, highly refractive liquid. When cooled below 5° C. it crystallizes in colorless crystals that melt at 5.4° C. Benzene has a specific gravity of .8784 at 20° C. and is soluble in alcohol and ether but insoluble in water. It burns with a bright smoky flame, has a peculiar ethereal odor, and boils at 80.4° C. It is used as a solvent for resins and fats. Commercially, benzene is known as *benzol*.

12. Structure of Benzene.—The saturated aliphatic hydrocarbons have the general formula C_nH_{2n+2}, and form substitution products only. On the other hand, hydrocarbons such as the olefines, which contain less hydrogen in proportion to carbon, form addition products. Benzene and other hydrocarbons of the series are represented by the formula C_nH_{2n-6}, which apparently indicates that benzene is an unsaturated hydrocarbon and will form addition products as do the olefines or acetylenes. Hence it is logical to assume that benzene will take up bromine and form the saturated compound *octobromhexane:*

$$C_6H_6+Br_8=C_6H_6Br_8;$$

or form *tetrabromhexane* by uniting with hydrobromic acid;

$$C_6H_6+4HBr=C_6H_{10}Br_4;$$

or unite with hydrogen and form the hydrocarbon hexane:

$$C_6H_6+8H=C_6H_{14}$$

None of these reactions, however, takes place. Bromine acts very readily but the action is one of substitution like that with the paraffins, and not one of addition. Hydrobromic acid, although reacting readily enough with the unsaturated hydrocarbons, has no effect on benzene. Bromine, under ordinary conditions, forms monobrombenzene, C_6H_5Br; in direct sunlight it forms *benzene hexabromide*, $C_6H_6Br_6$, and no more bromine can be added to this compound. Hydriodic acid reacts with benzene to form *benzene hexahydride*:

$$C_6H_6+6HI=C_6H_{12}+3I_2$$

This compound, while isomeric with the olefine *hexylene*, is not a member of the olefine series and when heated with an excess of hydriodic acid does not become hexane, C_6H_{14}, as does hexylene.

It appears, then, that benzene differs in some manner from all the preceding hydrocarbons, and other facts must be presented in order to form a hypothesis in regard to its structure. A study of the various substitution products of benzene soon furnishes very important facts of an entirely different order.

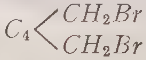
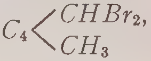
13. It will be remembered that the theory in regard to methane is that each hydrogen atom bears the same relation to the carbon atom and that methane is a symmetrical compound. The monosubstitution products of methane bear out this theory, and it is known that there is only one chlormethane, and only one brommethane. This is true of all the monosubstitution products of all the paraffins. A similar conclusion, based on a most careful study of the substitution products, has also been reached in regard to benzene. All efforts to obtain isomeric monosubstitution products of benzene have failed; there is but one monobrom, monochlor, or other monosubstitution product of benzene. Monobrombenzene has been prepared by substituting bromine for each successive atom of hydrogen in benzene; but the product obtained has always been the same regardless of which hydrogen atom has been replaced.

14. Suppose that C_6H_6, the formula for benzene, is written $C_6\overset{1}{H}\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$ and the hydrogen atoms numbered for the sake of easy reference. The problem now is to replace each hydrogen atom successively by bromine and then to compare the six products obtained. If bromine acts on benzene, one hydrogen atom is replaced by bromine forming monobrombenzene. It is not known which atom of hydrogen is replaced, but assuming it to be $\overset{1}{H}$, the compound will have the formula $C_6Br\overset{2}{H}\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. If, now, the compound is treated with nitric acid, another atom of hydrogen will be replaced by the nitro group. Although it is not known which atom of hydrogen will be replaced, it is known that it must be another than that replaced by the bromine, and assuming it to be $\overset{2}{H}$, the compound will have the formula $C_6BrNO_2\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. By the action of nascent hydrogen on this substance the bromine is replaced by hydrogen and the nitro group is converted into the amino group, giving a compound of the formula $C_6\overset{1}{H}(NH_2)\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$. The amino group can now be replaced by bromine and the result is a monobrombenzene of the formula $C_6\overset{1}{H}Br\overset{3}{H}\overset{4}{H}\overset{5}{H}\overset{6}{H}$, in which the bromine has replaced a different atom of hydrogen from that replaced by the bromine in the first instance. The two products, however, are identical. This principle has been applied to all the hydrogen atoms of the benzene molecule with exactly the same result, proving that all of the hydrogen atoms bear the same relation to the molecule, and the same is true of the carbon atoms, as the compound is symmetrical.

15. The question now arises as to how the six carbon atoms and the six hydrogen atoms can be arranged so that all will bear the same relation to the molecule. It has just been shown that the six hydrogen atoms are equal; hence three formulas, in which the six hydrogen atoms are of equal value, can be written for benzene. They are,

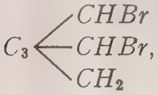
$$\underset{(1)}{C_4(CH_3)_2} \qquad \underset{(2)}{C_3(CH_2)_3} \qquad \underset{(3)}{(CH)_6}$$

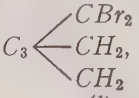
Further investigation of the chemical behavior of the benzene molecule discloses a second fact that concerns the disubstitution products of benzene. Thus, when two atoms of a halogen, as bromine, for instance, are substituted for two of the hydrogen atoms of benzene, it has been found that it is possible to form three isomeric dibrombenzenes. To determine which, if any, of the formulas numbered (1), (2), and (3) will yield three dibrombenzenes, the following substitutions are made:

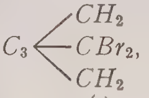
Formula (1), $C_4(CH_3)_2$, yields  $C_4\left\langle\begin{matrix}CH_2Br\\CH_2Br\end{matrix}\right.$ and  $C_4\left\langle\begin{matrix}CHBr_2,\\CH_3\end{matrix}\right.$

or only two disubstitution products.

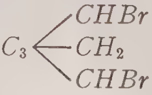
With formula (2) it would seem at first glance that four isomerides are possible. Thus, on substituting bromine for hydrogen the following formulas are obtained:


$C_3\left\langle\begin{matrix}CHBr\\CHBr,\\CH_2\end{matrix}\right.$
(*a*)


$C_3\left\langle\begin{matrix}CBr_2\\CH_2,\\CH_2\end{matrix}\right.$
(*b*)


$C_3\left\langle\begin{matrix}CH_2\\CBr_2,\\CH_2\end{matrix}\right.$
(*c*)

or


$C_3\left\langle\begin{matrix}CHBr\\CH_2\\CHBr\end{matrix}\right.$
(*d*)

On close inspection, however, it is seen that since all of the hydrogen atoms are of equal value, the compounds represented by formulas (*a*) and (*d*) are the same as are those represented by formulas (*b*) and (*c*). Thus formula (2) yields only two isomerides. Formula (3), $(CH)_6$, or C_6H_6, in which each carbon atom is connected to a hydrogen atom, offers greater possibilities, however.

16. The problem is then to write for benzene a formula that agrees with all of the facts, concerning its chemical behavior, that have been mentioned. Thus, the accepted formula must indicate that all of the hydrogen atoms of benzene are of equal value; it must show that three and only three isomeric disubstitution products are possible; but it must not indicate unsaturation, in the sense that the term is applied to the olefines, acetylenes, etc., since benzene does not behave as an unsaturated compound. The formula that best represents these facts is written in the form of a hexagon, as shown in Fig. 1, in which the positions of the carbon atoms are numbered for reference purposes. When one atom of bromine is substituted for hydrogen in this formula, it makes no difference which hydrogen atom is replaced, since the resulting compound will always be the same. Thus, the formulas shown in Fig. 2 represent the same compounds, and since positions 5 and 6 of the carbon atom correspond to positions 2 and 3, replacement of the hydrogen atoms connected to carbon at these points will result in the same compound, monobrombenzene, of which one only has been prepared.

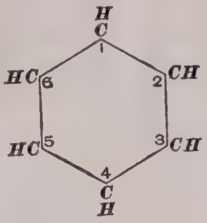


FIG. 1

17. The formulas shown in Fig. 2 represent the fact that all of the hydrogen atoms of benzene are of equal value. When two atoms of bromine are substituted for two atoms of hydrogen, as shown in the formulas of Fig. 3, it is seen that the bromine atoms in (*a*) and (*b*) are connected to adjacent carbon atoms at 1–2 and 1–6. Therefore, formulas (*a*) and (*b*) represent the same dibrombenzene. In formulas (*c*) and (*d*) bromine is substituted for hydrogen at positions 1–3 and 1–5. These two formulas represent the same compound; but it is different from that represented by formulas (*a*) and (*b*).

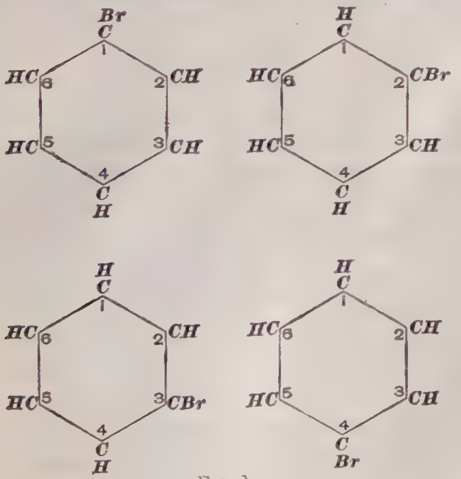


FIG. 2

Thus, the formulas for two of the isomeric disubstitution products of benzene have been represented by means of the hexagon formula for benzene. In formula (*e*) the hydrogen atoms at positions 1–4 have been replaced by bromine, and the compound formed is different in structure from those represented by formulas (*a*), (*b*), (*c*), and (*d*); thus, the formula of the third isomeric dibrombenzene is written as shown in (*e*).

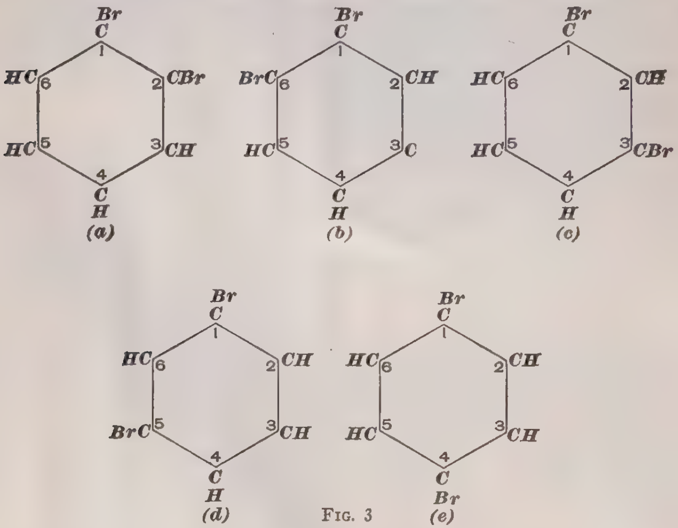


FIG. 3

18. The third fact that the formula for benzene must represent is that the molecule is not unsaturated in the usual meaning of the word. At the same time the formula must account for addition products, such as $C_6H_6Br_6$, which is regarded as being unsaturated, since the saturated bromine compound has the formula $C_6H_6Br_8$. Many prominent investigators, among whom may be mentioned Kekulé, Ladenburg, Claus, Armstrong, Baeyer, and Thiele, have attempted to modify the hexagon or ring formula for benzene in such a manner that the peculiar unsaturation that does exist in the molecule will be represented. None of these investigators, however, has been entirely successful in advancing a plausible explanation that completely meets all requirements.

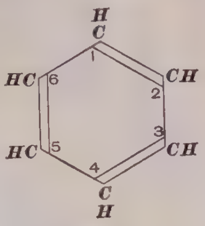
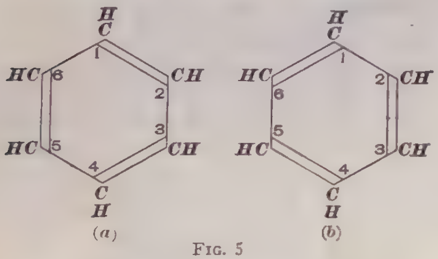


FIG. 4



(*a*) (*b*)

FIG. 5

19. Kekulé Formula.—The ring or hexagon formula for benzene, as far as it has been developed in the present discussion, shows each carbon atom connected to only three other atoms, which apparently indicates that carbon in benzene is trivalent. This, however, does not agree with the great mass of evidence that may be assembled to support the idea of the tetravalency of carbon. To overcome this objection to the ring formula for benzene, Kekulé introduced the double bond in the formula as shown in Fig. 4. In this formula, the four valences of each carbon atom are satisfied. However, while the modified formula takes care of one difficulty, it introduces another. Thus, it will be noted that the disubstitution products obtained by the introduction of bromine, for instance, at positions 1–2 and 1–6 cannot now be the same, since the carbon atoms at 1–2 are now connected by a double bond and those at 1–6 are connected by a single bond. To remedy this defect in the formula, Kekulé suggested that the double bonds are not fixed, but that they are free to oscillate, so that at one instant they occupy the positions shown in Fig. 5 (*a*) and the next instant the positions shown in (*b*). Recent investigations have given support to Kekulé's oscillation theory.

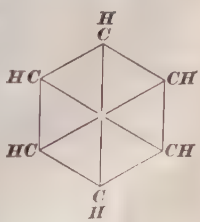


FIG. 6

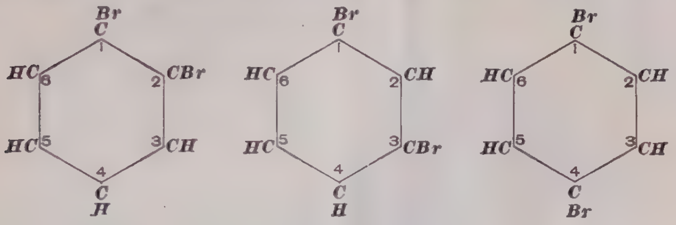
20. Armstrong-Baeyer Centric Formula. The oscillation theory of Kekulé not being acceptable to them, Armstrong and Baeyer devised the so-called *centric formula* illustrated in Fig. 6. In the centric formula the fourth valence of each of the carbon atoms is directed toward the center of the ring. This configuration is designed to indicate that the fourth valence of any one carbon atom is rendered latent and not permanently satisfied nor destroyed by the valences of the other carbon atoms. This theory accounts for the fact that under certain conditions benzene acts as a saturated compound and under other conditions as an unsaturated compound.

None of the several formulas developed to show the structure of the benzene molecule fully meets all requirements, however, and until the matter is finally settled to the complete satisfaction of all chemists, the simple ring formulas of Figs. 1, 2, and 3 will be used.

NOMENCLATURE OF BENZENE DERIVATIVES

21. Disubstitution Products.—In order to distinguish between the isomeric disubstitution products of benzene, the prefixes *ortho-*, *meta-*, and *para-* are used in naming them. These prefixes serve to indicate the exact position occupied in the benzene ring, by the substituted atom. As previously stated, the hydrogen atoms of benzene are all of equal value. Therefore, the compound formed, when any two hydrogen atoms that are next to each other in the ring are replaced, is always the same. Thus, when bromine is substituted for hydrogen at positions 1–2, 2–3, 3–4, 4–5, 5–6, or 1–6, the same compound, dibrombenzene, is formed; and to distinguish it from the other two isomeric disubstitution products it is called ortho-dibrombenzene. When the hydrogen atoms at positions 1–3, 2–4, 3–5, 4–6, 5–1, and 6–2 are replaced, another isomeric disubstitution product results that differs from the ortho compound. It is called a meta compound. In a similar manner, when the hydrogen atoms at positions 1–4, 2–5, and 3–6 are replaced, the resulting compound is called a para compound. The foregoing may be summarized as follows: When *adjacent* hydrogen atoms in the benzene ring are replaced by other atoms, groups of atoms, or radicals, the result is an ortho compound; when *alternate* atoms are replaced, the result is a meta compound; and when *opposite* atoms are replaced, the result is a para compound. The formulas for ortho-, meta-, and para-dibrombenzene are illustrated in Fig. 7.

In another method of naming the isomeric disubstitution products of benzene, the numbers indicating the positions of the replaced hydrogen atoms are used. Thus, ortho-, meta-, and para-dibrombenzene are also called 1–2 dibrombenzene, 1–3 dibrombenzene, and 1–4 dibrombenzene.



ortho-dibrombenzene
or
1–2 dibrombenzene

meta-dibrombenzene
or
1–3 dibrombenzene

para-dibrombenzene
or
1–4 dibrombenzene

FIG. 7

22. Polysubstitution Products.—When three similar atoms are substituted for hydrogen in benzene, three isomeric compounds result. They are known as adjacent, or *vicinal*, when the substitution takes place at 1–2–3, or 2–3–4, etc.; as *symmetrical* when substitution takes place at 1–3–5, etc.; and as *unsymmetrical* when substitution takes place at 1–3–4. When one of the radicals is different from the other two, different vicinal derivatives will result by substituting at 2 and 3, respectively, and for the unsymmetrical compound, substitution at 3 produces a different compound from that resulting by substitution at 4. For four similar substituting radicals three isomerides are possible: adjacent (1–2–3–4), symmetrical (1–2–4–5), and unsymmetrical (1–3–4–5), and with different radicals the number of isomeric compounds increases rapidly.

ORIENTATION

23. The determination of the relative positions occupied by the substituting atoms or radicals in the benzene ring is called *orientation*. Thus, given the three isomeric dibrombenzenes, how can it be determined which of them is the ortho compound, which the meta compound and which the para compound?

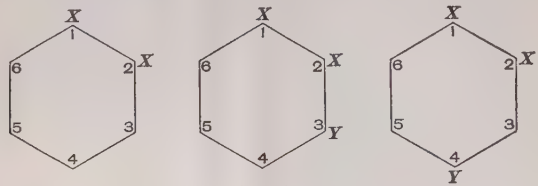


FIG. 8

The orientation of the benzene derivatives is carried out by attempting to introduce new radicals into the benzene ring or in replacing an already substituted radical by hydrogen. The general method is that of Korner, by which it is possible to ascertain whether compounds containing two substituents are ortho, meta, or para compounds by determining the number of trisubstitution products corresponding to them.

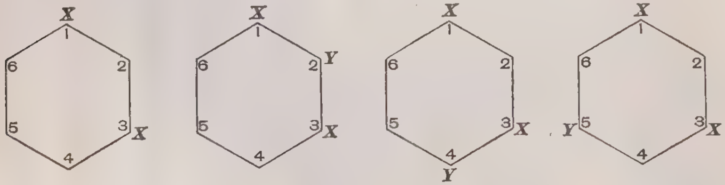


FIG. 9

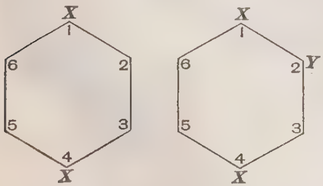


FIG. 10

When a third radical is introduced in an ortho compound, regardless of whether it is the same as, or different from the other substituents, only two isomerides are possible, as shown in Fig. 8. A meta compound under the same conditions yields three isomerides, as shown in Fig. 9. The introduction of the third group into a para compound, on the other hand, forms only one trisubstitution product, as shown in Fig. 10. Hence, it is evident that, of three disubstitution products, the one yielding two trisubstitution products must be the 1–2 compound, the one yielding three must be the 1–3 compound, and the one yielding only one trisubstitution product must be the 1–4 compound.

24. The orientation of the trisubstituted and higher substituted derivatives is usually effected by ascertaining the relation in which they stand to the disubstitution derivatives of known constitution. This is done by replacing a substituent by hydrogen and thus obtaining one or more disubstitution derivatives. If the tri- derivative is a 1–2–3 compound it will yield two di- derivatives, namely, 1–2 and 1–3; if it is a 1–3–4 compound it will yield three di- derivatives; and if a 1–3–5 compound, it can yield only one di- derivative.

The orientation of certain derivatives having been settled by investigations involving the preceding principles, these may be termed standard derivatives, and the orientation of a new compound settled by converting it into one of these. The most generally used of these standards are the bromo derivatives and the carboxylic acids. Thus, the orientation of a newly discovered nitro derivative could be settled by converting it into bromo derivatives, a study of which would decide its orientation and consequently that of the original nitro derivative.

HOMOLOGUES OF BENZENE

TOLUENE, $C_6H_5 \cdot CH_3$

25. Introductory.—The homologues of benzene may be considered as derivatives of benzene in which the hydrogen of the benzene has been replaced by alkyl radicals, such substituted radicals being known as *side chains*. In what follows, the benzene ring will be referred to as the *nucleus*. Thus, in the formula for toluene, $C_6H_5 \cdot CH_3$, the group C_6H_5 is known as the *phenyl radical* and when combined with the methyl radical CH_3, the phenyl radical becomes the nucleus and the methyl radical the side chain.

26. Preparation of Toluene.—Toluene is obtained when a gummy or resinous substance called *balsam of tolu* is destructively distilled. It is also present in the oils obtained by distilling coal tar. It may be prepared by making use of *Fittig's synthesis*, which consists in bringing together in ethereal solution and in the presence of metallic sodium, a phenyl halide and an alkyl halide. In the preparation of toluene, brombenzene, methyl bromide, and metallic sodium are brought together. The reaction that takes place is represented by the following equation:

$$C_6H_5Br+CH_3Br+2Na=C_6H_5 \cdot CH_3+2NaBr$$

Toluene is also prepared by the reaction of Friedel and Craft, which consists in causing a reaction to take place between a benzene hydrocarbon and an alkyl halide in the presence of anhydrous aluminum chloride. In the case of toluene the reaction is represented as follows:

$$C_6H_6+CH_3Cl=C_6H_5 \cdot CH_3+HCl$$

Zinc chloride and ferric chloride act in a similar manner. It is very probable that an organo-metallic compound is first formed and that this then reacts with the alkyl chloride; thus,

$$C_6H_6+AlCl_3=C_6H_5 \cdot AlCl_2+HCl$$
$$C_6H_5 \cdot AlCl_2+CH_3Cl=C_6H_5 \cdot CH_3+AlCl_3$$

27. Properties.—Toluene may be considered as *methyl benzene*, or benzene with one atom of hydrogen replaced with methyl, or as *phenyl methane*, or methane in which one atom of hydrogen is replaced by phenyl.

Toluene is a colorless, refractive liquid with a benzene-like odor; it boils at 110° C. and has a specific gravity of .8625 at 25° C. It is soluble in alcohol and ether but only slightly soluble in water. Toluene is used in the manufacture of coal-tar dyes and explosives, and in the preparation of artificial musk. It is very susceptible to the action of reagents, and yields a large number of substitution products, some of which are very important.

Oxidizing agents act on toluene in a peculiar manner. The methyl radical is oxidized and the phenyl radical remains unacted on. The product of oxidation is benzoic acid, as represented by the equation

$$C_6H_5 \cdot CH_3 + 3O = C_6H_5 \cdot COOH + H_2O$$

Only one toluene or methyl benzene has ever been discovered.

XYLENES, $C_6H_4 \cdot (CH_3)_2$

28. The xylenes, or dimethyl benzenes, exist in three isomeric forms, *ortho-xylene*, *meta-xylene*, and *para-xylene*. That part of the light oil obtained from coal tar boiling between 137° C. and 143° C. was originally called xylene, but it was later found to consist of the three forms. The xylenes are very difficult to separate, as their boiling points are nearly the same. They may be separated, however, by treating them with sulphuric acid at ordinary temperatures, when meta-xylene and ortho-xylene go into solution as sulphonic acids, and para-xylene is unaffected. The sodium salts of the ortho-meta-sulphonic acids are then separated by fractional crystallization, the ortho salt crystallizing first.

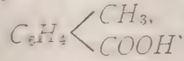
Ortho-xylene, or ortho-dimethylbenzene, $C_6H_4(CH_3)_2$[1–2] is a colorless liquid closely resembling benzene and toluene in its general properties. It boils at 142° C. and has a specific gravity of .893.

Meta-xylene, or meta-dimethylbenzene, $C_6H_4(CH_3)_2$[1–3], is a colorless liquid boiling at 139° C. and having a specific gravity of .881.

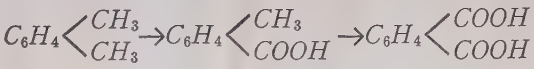
Para-xylene, or para-dimethylbenzene, $C_6H_4(CH_3)_2$[1–4], is a colorless liquid above 15° C. It boils at 138° C. and has a specific gravity of .862.

The three xylenes are also obtained by treating ortho-, meta-, or para-bromtoluene with methyl iodide and sodium.

On oxidation the xylenes undergo the same change as toluene, namely, the methyl radical only is acted on and is converted into carboxyl. The first product of oxidation is to form a toluic acid, $C_6H_4 \langle {CH_3, \atop COOH}$, corresponding to the xylene. Fur-



ther oxidation converts the remaining methyl group into carboxyl, forming ortho-, meta-, or para-phthalic acid,



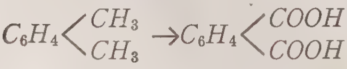
$$C_6H_4\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}CH_3\\COOH\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$$

ETHYL BENZENE, $C_6H_5 \cdot C_2H_5$

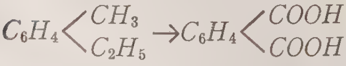
29. Ethyl benzene, although isomeric with the xylenes, differs from them in that it contains an ethyl group in place of one hydrogen atom, while the xylenes contain two methyl groups replacing two hydrogen atoms of benzene. Ethyl benzene is prepared by treating brombenzene and ethyl bromide with sodium. It is best prepared, however, by the action of ethyl chloride on benzene in the presence of aluminum chloride.

Oxidizing agents serve to distinguish between ethyl benzene and the xylenes. Ethyl benzene, when oxidized, yields benzoic acid, as does toluene. It has been found that no matter what paraffin radical has replaced hydrogen in benzene, it is this paraffin radical that is converted into carboxyl by oxidizing agents. Thus, the following conversions are the result of oxidation of the aromatic hydrocarbons:

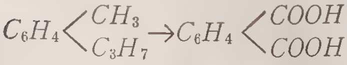
$$C_6H_5 \cdot CH_3 \rightarrow C_6H_5 \cdot COOH$$
$$C_6H_5 \cdot C_2H_5 \rightarrow C_6H_5 \cdot COOH$$
$$C_6H_5 \cdot C_3H_7 \rightarrow C_6H_5 \cdot COOH$$
$$C_6H_5 \cdot C_5H_{11} \rightarrow C_6H_5 \cdot COOH$$



$$C_6H_4\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$$



$$C_6H_4\left\langle\begin{matrix}CH_3\\C_2H_5\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$$



$$C_6H_4\left\langle\begin{matrix}CH_3\\C_3H_7\end{matrix}\right. \rightarrow C_6H_4\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right.$$

TRIMETHYL BENZENES, $C_6H_3 \cdot (CH_3)_3$

30. Isomerides.—Three isomeric trimethyl benzenes are possible and all three compounds are known. They are: mesitylene, or symmetrical 1–3–5 trimethyl benzene; pseudo-cumene, or unsymmetrical 1–3–4 trimethyl benzene; and hemelithene, or vicinal 1–2–3 trimethyl benzene.

31. Mesitylene, $C_6H_3\cdot(CH_3)_3$.—Mesitylene is obtained in small quantities from the light oil obtained by distilling coal tar. It may be prepared by heating acetone with sulphuric acid. Thus,

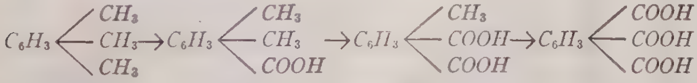
$$3CH_3\cdot CO\cdot CH_3 = C_6H_3\cdot(CH_3)_3 + 3H_2O$$

The sulphuric acid merely serves to remove the three molecules of water from three molecules of acetone and may be recovered unchanged. Mesitylene can also be obtained by a method analogous to the polymerization of acetylene, namely, treating methyl acetylene with sulphuric acid; thus,

$$3CH_3C\equiv CH = C_6H_3\cdot(CH_3)_3$$

Mesitylene is a colorless, oily liquid, with a peculiar odor. It is soluble in alcohol, ether, and benzene, boils at 164° C., and has a specific gravity of .865.

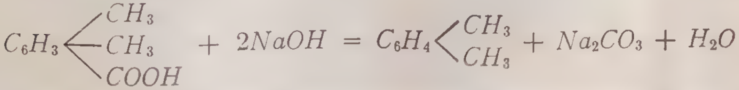
32. Structure of Mesitylene.—The conduct of mesitylene toward oxidizing agents shows it to be trimethyl benzene. Treated with nitric acid, it forms successively *mesitylenic acid, uvitic acid*, and *trimesitic acid;* thus



$$C_6H_3\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\rightarrow C_6H_3\begin{matrix}CH_3\\CH_3\\COOH\end{matrix}\rightarrow C_6H_3\begin{matrix}CH_3\\COOH\\COOH\end{matrix}\rightarrow C_6H_3\begin{matrix}COOH\\COOH\\COOH\end{matrix}$$

mesitylene mesitylenic acid uvitic acid trimesitic acid

These products of oxidation show clearly that mesitylene is trimethyl benzene but they do not prove it to be symmetrical. It has been assumed to be symmetrical from the fact that when mesitylenic acid, which is formed as the result of the oxidation of one CH_3 group, is heated with caustic soda, it loses carbon dioxide and is converted into meta-xylene, or 1–3 dimethyl benzene. Thus,



$$C_6H_3\begin{matrix}CH_3\\CH_3\\COOH\end{matrix} + 2NaOH = C_6H_4\begin{matrix}CH_3\\CH_3\end{matrix} + Na_2CO_3 + H_2O$$

Therefore, assuming that the methyl groups do not change their positions, it is evident that mesitylene is a symmetrical compound, since it can only be a 1–3–5 compound that can give rise to a 1–3 compound by the foregoing reactions.

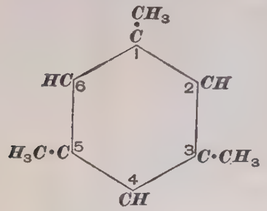


FIG. 11

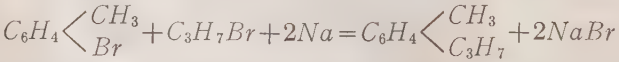
In the preparation of mesitylene by treating acetone with sulphuric acid, it is assumed that from each molecule of acetone, $CH_3\cdot CO\cdot CH_3$, one molecule of H_2O is removed, leaving three unsaturated residues, CH_3-C-CH, to combine to form mesitylene. The only way in which this combination can be represented is shown by the formula for mesitylene, Fig. 11.

33. Pseudo-Cumene and Hemelithene.—Pseudo-cumene is obtained from coal tar and has a boiling point of 169.5° C. and a specific gravity of .8764. Hemelithene is also obtained from coal tar and is similar to mesitylene and pseudo-cumene in most of its properties. It boils at 175° C.

CYMENE, $C_6H_4<\begin{matrix}CH_3(1)\\C_3H_7(4)\end{matrix}$

34. Cymene, or para-methyl isopropyl benzene, is closely related to the terpenes and camphors from which it can be obtained. It occurs in certain essential oils, such as oil of caraway, oil of thyme, and oil of eucalyptus.

The easiest way to obtain cymene is to treat camphor with zinc chloride or phosphorus pentoxide. It can be prepared synthetically in the usual way from para-bromtoluene and isopropyl bromide by means of the reaction,

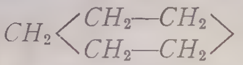


$$C_6H_4<\begin{matrix}CH_3\\Br\end{matrix}+C_3H_7Br+2Na=C_6H_4<\begin{matrix}CH_3\\C_3H_7\end{matrix}+2NaBr$$

Cymene is a transparent, colorless liquid, with a pleasant, aromatic odor. It is soluble in alcohol, boils at 175° C., and has a specific gravity of .856. Oxidizing agents convert cymene into para-phthalic acid.

HEXAHYDROBENZENES, OR NAPHTHENES

35. General Properties.—A number of compounds occur in nature that contain hydrogen in a proportion intermediate between that of the aromatic derivatives with saturated side chains and that of the saturated aliphatic derivatives. These hydrocyclic, or hydroaromatic, compounds are readily converted into aromatic substances by passing them through red-hot tubes. They differ from the benzene hydrocarbons in that they do not react with concentrated nitric or sulphuric acid. These compounds are called *napthenes*, and have the general formula C_nH_{2n}. Although these substances have two atoms of hydrogen less than the corresponding saturated hydrocarbons, they display all of the characteristic properties of saturated compounds. The explanation of this is that they lack multiple bonds, but consist of a closed carbon chain.

36. Hexamethylene,  $CH_2\left\langle\begin{matrix}CH_2{-}CH_2\\ CH_2{-}CH_2\end{matrix}\right\rangle CH_2$.—Hexamethylene is the simplest member of the hexahydrobenzene group. It is found in Caucasian petroleum, and in small quantities in American petroleum. It is best obtained by the Sabatier and Senderens method. This consists in passing the vapors of benzene mixed with hydrogen over heated, finely divided nickel obtained by the reduction of the oxide. This finely divided and highly heated nickel exerts a catalytic action. The method is also applicable to the homologues of benzene.

Hexamethylene is a colorless liquid that boils at 80° C. and solidifies below 6° C. As its boiling point is very close to that of benzene (80.4° C.), it is impracticable to separate it from the benzene, with which it is mixed, by fractional distillation. Advantage is taken of its stability at the ordinary temperature to concentrated nitric and sulphuric acids. These convert benzene into nitrobenzene and benzene sulphonic acid. As the hexamethylene is insoluble in either of these acids and the benzene compound is easily soluble in the corresponding acid, the separation is readily effected.

Chlorine reacts very energetically with hexamethylene in diffused sunlight, and with explosive violence in direct sunlight.

DERIVATIVES OF BENZENE SERIES

PRELIMINARY REMARKS

37. In the course of the study of the paraffin derivatives it was found that five classes of derivatives were obtained, namely: (1) Halogen derivatives; (2) oxygen derivatives; (3) sulphur derivatives; (4) nitrogen derivatives; (5) metallic derivatives.

With the benzene hydrocarbons, the same classes of derivatives are obtained, but owing to the many points of analogy between the halogen substitution products, the nitro compounds and the sulphonic acids, a slightly different order of treatment is an advantage in studying these derivatives. These three classes are derived by the direct treatment of the hydrocarbons with the substituting agent. The amino derivatives of this series are obtained almost exclusively by reducing the nitro compounds, and they naturally follow them. Again, the action of nitrous acid on the amino compounds gives rise to a new class of nitrogen derivatives not met with in connection with the paraffins, namely, the diazo compounds. Hence the following classes of benzene derivatives:

1. Halogen derivatives.
2. Nitro compounds, including the amino and diazo compounds.
3. Sulphonic acids.
4. Oxygen derivatives—the phenols, alcohols, aldehydes, acids, ketones, and quinones.
5. Hydroxy acids.

These classes of derivatives bear practically the same relations to the hydrocarbons as the corresponding derivatives of the paraffin series do to the paraffins. As the general methods of formation and the reactions are the same, the knowledge acquired in the study of the paraffin series can be applied to this series. Although an enormous number of derivatives of the benzene hydrocarbons have been prepared, only the most important will be described.

HALOGEN DERIVATIVES OF BENZENE AND ITS HOMOLOGUES

ADDITION PRODUCTS

38. When either chlorine or bromine acts on benzene in the presence of sunlight the addition products benzene hexachloride, $C_6H_6Cl_6$, and benzene hexabromide, $C_6H_6Br_6$, are formed. These products, however, decompose and form halogen acids and trisubstitution products of benzene. Thus, when benzene hexachloride decomposes, trichlorbenzene and hydrochloric acid are formed. The reaction is represented as follows:

$$C_6H_6Cl_6 = C_6H_3Cl_3 + 3HCl$$

SUBSTITUTION PRODUCTS

39. Introductory.—Chlorine and bromine unite directly with benzene, in the presence of diffused daylight, to form substitution products. The reaction takes place slowly, however, and is greatly accelerated by the presence of so-called halogen carriers, such as aluminum chloride, ferric chloride, iodine, sulphur, phosphorus, and iron. Substitution of iodine into the benzene ring is effected only in the presence of an oxidizing agent.

40. The substitution products of the benzene series are very stable. They are more easily formed and are more difficult to decompose than those of the paraffins. While it is possible to replace the halogen in a paraffin derivative with hydroxyl or the amino group, it is more difficult to effect these replacements in the benzene derivatives. The halogens can, however, be removed by sodium, as in the synthesis of the hydrocarbons. This can be accomplished also by nascent hydrogen; thus,

$$C_6H_5Cl + H_2 = C_6H_6 + HCl$$

This reverse substitution, however, is effected only with considerable difficulty.

41. The reactions between benzene and the halogens to form substitution products are not clean-cut in so far as the products obtained are concerned. The reaction between bromine and benzene in the presence of a halogen carrier to form monobrombenzene may be represented by the equation

$$C_6H_6 + Br_2 = C_6H_5Br + HBr$$

In practice, however, all of the benzene is never converted to the halogen derivative, and the product formed as the result of the reaction does not consist solely of a monohalogen compound. On the other hand, it is possible for the product obtained to consist of a mixture of substitution products that contain from 1 to 6 atoms of the halogen. Excessive halogenation may usually be avoided, however, by keeping the temperature of the reaction low and by avoiding the use of an excess of the halogen.

The products obtained when the hydrocarbon is treated with a halogen may usually be separated from each other by fractional distillation or fractional crystallization.

The halogen derivatives of benzene and of some of its homologues are of little practical importance and only a few methods of preparation will be described to show how the halogens are introduced into the benzene ring and the effect of certain conditions in determining the number of atoms introduced.

42. Brombenzenes.—The bromine substitution products of benzene are prepared by the action of bromine on benzene in the presence of a halogen carrier. The names of the brombenzenes that are possible, together with their formulas, boiling points, and melting points, are given in Table III. The numbers that follow the names of the different derivatives refer to the positions of the substituted atoms in the benzene ring.

When benzene is treated with bromine under the conditions given, that is, in the presence of a halogen carrier, the principal product obtained with the theoretical quantity of halogen is the monohalogen derivative. When the quantity of bromine used is that required for a disubstitution product, the principal derivative obtained is para-dibrombenzene, and only a small quantity of the ortho derivative is formed, The meta derivative is never formed under the conditions given.

TABLE III

POSSIBLE BROMBENZENES

Name	Formula	Boiling Point Degrees C.	Melting Point Degrees C.
Monobrombenzene	C_6H_5Br	155	−31
Ortho-dibrombenzene (1–2)	$C_6H_4Br_2$	224	− 1
Meta-dibrombenzene (1–3)		219	+ 1
Para-dibrombenzene (1–4)		219	89
Vicinal tribrombenzene (1–2–3)	$C_6H_3Br_3$		87
Unsymmetrical tribrombenzene (1–2–4)		275	44
Symmetrical tribrombenzene (1–3–5)		278	120
Vicinal tetrabrombenzene (1–2–3–4)	$C_6H_2Br_4$		
Unsymmetrical tetrabrombenzene (1–2–3–5)		329	98
Symmetrical tetrabrombenzene (1–2–4–5)			175
Pentabrombenzene	C_6HBr_5		260
Hexabrombenzene	C_6Br_6		320

43. Preparation of Monobrombenzene and Dibrombenzene.—Monobrombenzene and dibrombenzene may be prepared by bringing together in a 250 cubic centimeter flask, 50 grams of benzene, and 120 grams (40 cubic centimeters) of bromine and from .5 to 1 gram of the halogen carrier, which may be coarse iron filings. The flask is fitted with a reflux condenser and is placed in an ice-water bath. The top of the condenser contains a two-hole stopper that carries a dropping funnel for the introduction of bromine and a delivery tube through which passes the hydrobromic acid gas evolved by the reaction and which is absorbed in water.

The operation is carried out by placing the benzene and the halogen carrier in the flask on the ice-water bath. The condenser is then connected to the flask and the bromine added. If the reaction does not start within a few minutes, as is indicated by the non-evolution of hydrobromic acid gas, the ice-water bath is temporarily removed and the temperature of the contents of the flask is permitted to rise. When the reaction begins, the ice-water bath is at once placed in contact with the reaction flask; otherwise, the temperature would rise and the reaction would take place too vigorously. When the reaction has greatly subsided,the ice-water bath is permanently removed and the contents of the flask slowly heated until a temperature of 70° C. is reached. The temperature is then kept at this point until the evolution of hydrobromic acid gas has practically ceased. The contents of the flask are now cooled and washed several times with a 5 per cent. solution of sodium hydroxide and then distilled with steam. This method of distillation is carried out by boiling water in another flask and conducting the steam so generated into the flask containing the mixture to be distilled. The reaction flask is connected to a condenser in the same manner as before the steam is passed into it. Benzene and liquid monobrombenzene are collected in the receiver and when crystals of solid dibrombenzene appear in the condenser, the receiver is changed and the distillation continued until all of the dibrombenzene has distilled. The monobrombenzene in the first receiver is separated from most of the water by means of a separatory funnel, dried with anhydrous calcium chloride and then fractionally distilled. The fraction taken should distill between 140° and 170° C. It is then redistilled and the portion passing over between 150° and 160° C. is collected. Pure monobrombenzene boils at 155° C., and the fractionation is continued, the boiling range being decreased for each distillate until a product that has a boiling point of approximately 155° C. is obtained. The crystals of dibrombenzene that have formed in the second receiver are dissolved in alcohol and recrystallized. Pure dibrombenzene melts at 89° C.

TABLE IV

CHLORINE DERIVATIVES OF BENZENE

Name	Formula	Boiling Point Degrees C.	Melting Point Degrees C.
Monochlorbenzene	C_6H_5Cl	132	−45
Ortho-dichlorbenzene (1–2)	$C_6H_4Cl_2$	179	
Meta-dichlorbenzene (1–3)		172	
Para-dichlorbenzene (1–4)		172	53
Vicinal trichlorbenzene (1–2–3)	$C_6H_3Cl_3$	218	16
Unsymmetrical trichlorbenzene (1–2–4)		213	63
Symmetrical trichlorbenzene (1–3–5)		208	54
Vicinal tetrachlorbenzene (1–2–3–4)	$C_6H_2Cl_4$	254	46
Unsymmetrical tetrachlorbenzene (1–2–3–5)		246	50
Symmetrical tetrachlorbenzene (1–2–4–5)		244	137
Pentachlorbenzene	C_6HCl_5	276	86
Hexachlorbenzene	C_6Cl_6	326	226

44. Chlorbenzenes.—When benzene is treated with chlorine, the product obtained consists of a mixture of monochlorbenzene and the ortho and para derivatives, the quantity of each depending on the conditions under which the experiment is carried out. If the theoretical quantity of chlorine required for the formation of the monochlor compound is passed into the benzene with the reaction mixture exposed to light, the products obtained will consist for the most part of ortho- and para-dichlorbenzene and some unchanged benzene. If only one-half of the theoretical quantity of chlorine is used and chlorination is carried out with the reaction mixture at a temperature of about 40° C., and protected from the light, the maximum yield of monochlorbenzene will be obtained together with the minimum yields of ortho- and para-dichlorbenzene. The properties of the various chlorine derivatives of benzene are given in Table IV.

45. Preparation of Monochlorbenzene and Dichlorbenzene.—Monochlorbenzene and dichlorbenzene may be prepared by passing a current of dry chlorine into 250 grams of benzene at a temperature of 40° C., that contains about 5 grams of iron filings, until the increased weight of the reaction mixture amounts to about 80 grams. The reaction flask is fitted with a reflux condenser and is protected from the light. When the required quantity of chlorine has been passed into the benzene, the reflux condenser and chlorine delivery tube are detached from the reaction flask and the latter connected to a condenser in the regular way and its contents are fractionally distilled. That fraction distilling between 125° and 140° C. contains most of the monochlorbenzene and the remainder of the distillate most of the dichlorbenzenes.

Monochlorbenzene boils at 132° C., and the fraction boiling between 125° and 140° C. is further fractionated until a product having a boiling point approximating that of pure monochlorbenzene is obtained. The heavy fraction boiling above 140° C. is cooled and para-dichlorbenzene crystallizes. The mother liquor then consists largely of ortho-dichlorbenzene.

46. Iodobenzenes.—The iodine substitution products of benzene may be obtained by treating benzene with iodine in the presence of iodic acid or by treating benzene with iodine chloride in the presence of aluminum chloride. In the first instance, the reaction is represented by the equation

$$5C_6H_6+2I_2+HIO_3=5C_6H_5I+3H_2O$$

In the second method, iodobenzene dichloride is first formed,

$$C_6H_6+ICl_3=C_6H_5\cdot ICl_2+HCl$$

which when treated with caustic soda forms iodosobenzene,

$$C_6H_5\cdot ICl_2+2NaOH=C_6H_5\cdot IO+2NaCl+H_2O$$

and when iodosobenzene is treated with hydriodic acid, iodobenzene is obtained,

$$C_6H_5\cdot IO+2HI=C_6H_5I+I_2+H_2O$$

Iodobenzene is a liquid boiling at 188° C. The importance of the iodobenzenes lies in the fact that they form a group of derivatives that are not obtained from chlorine or bromine substitution products.

47. Iodobenzene Dichloride, $C_6H_5\cdot ICl_2$.—Iodobenzene dichloride or phenyliodoso chloride is formed when chlorine is passed into a chloroform solution of iodobenzene. It is a yellow crystalline compound that is slowly decomposed by a solution of potassium iodide with the formation of iodobenzene. Thus,

$$C_6H_5\cdot ICl_2+2KI=C_6H_5I+2KCl+I_2$$

48. Iodosobenzene, $C_6H_5\cdot IO$.—When iodobenzene dichloride is treated with a 5 per cent. solution of caustic soda it is slowly decomposed and a new compound, iodosobenzene, is formed. The same reaction takes place when water alone is used. Thus,

$$C_6H_5\cdot ICl_2+H_2O=C_6H_5\cdot IO+2HCl$$

49. Iodoxybenzene, $C_6H_5IO_2$.—When iodosobenzene is heated with water or is distilled with steam it decomposes with the formation of two compounds, one of which is iodobenzene, and the other, iodoxybenzene.

$$2C_6H_5\cdot IO=C_6H_5I+C_6H_5\cdot IO_2$$

When the aqueous solution of the latter is concentrated by evaporation and then cooled, crystals of iodoxybenzene are obtained. Iodoxybenzene decomposes with explosive violence when heated to about 230° C. It is an oxidizing agent.

50. Diphenyliodonium Hydroxide, $(C_6H_5)_2I{\cdot}OH$.—Diphenyliodonium hydroxide, known only in its aqueous solution, is prepared by treating a mixture of iodosobenzene and iodobenzene with moist silver oxide; thus,

$$C_6H_5{\cdot}IO+C_6H_5{\cdot}IO_2+AgOH=(C_6H_5)_2I{\cdot}OH+AgIO_3$$

Diphenyliodonium hydroxide is strongly alkaline and forms salts analogous to the thallium salts. It is sometimes regarded as the diphenyl derivative of a hypothetical base, iodonium hydroxide, $H_2I(OH)$, which bears the same relation to iodine that ammonium hydroxide does to nitrogen.

HALOGEN DERIVATIVES OF TOLUENE

51. Methods of Halogenation.—The homologues of benzene consist of one or more alkyl or aliphatic radicals substituted for hydrogen in the benzene molecule. Therefore, two classes of derivatives are possible, depending on whether the halogen atom enters the aliphatic radical or side chain, or whether it enters the benzene ring or nucleus. If halogenation is carried out in the cold, in the presence of halogen carriers, the halogen enters the benzene nucleus; but if the operation is carried out at the boiling point of the hydrocarbon, or under the influence of direct sunlight, the halogen enters the aliphatic radical or side chain.

52. Compounds Formed.—Under the conditions given, toluene, $C_6H_5CH_3$, yields the following substitution products with chlorine:

SUBSTITUTION IN NUCLEUS

$C_6H_4Cl{\cdot}CH_3$ (monochlortoluenes, *o*, *m*, and *p*)
$C_6H_3Cl_2{\cdot}CH_3$ (dichlortoluenes, *vic; sym;* and *unsym.*)
$C_6H_2Cl_3{\cdot}CH_3$ (trichlortoluenes)
$C_6HCl_4{\cdot}CH_3$ (tetrachlortoluene)
$C_6Cl_5{\cdot}CH_3$ (pentachlortoluene)

SUBSTITUTION IN SIDE CHAIN

$C_6H_5{\cdot}CH_2Cl$ (benzyl chloride)
$C_6H_5{\cdot}CHCl_2$ (benzal chloride)
$C_6H_5{\cdot}CCl_3$ (benzotrichloride)

In connection with these compounds, the different groups or radicals that enter into their structures and to the presence of which they and other derivatives owe their names, are pointed out. The names of the radicals with their formulas are: *benzyl*, $C_6H_5{\cdot}CH_2$; *benzylidene* or *benzal*, $C_6H_5{\cdot}CH$; and *benzenyl*, $C_6H_5{\cdot}C$. Thus, benzal chloride is also known as benzylidene chloride and benzotrichloride as benzenyl chloride.

53. Oxidation Products of Substituted Toluenes.—Distinction between the two classes of substituted toluenes is made easily because of the difference of their behavior on oxidation. When substitution is made in the nucleus, as in the case of the chlortoluenes, only the side chain is affected by oxidation, the nucleus remaining unchanged as in the case of toluene itself. The products obtained are known as substituted benzoic acids. Only the first two are given:

$C_6H_4Cl{\cdot}CH_3 \rightarrow C_6H_4Cl{\cdot}COOH$ (monochlorbenzoic acid)
$C_6H_3Cl_2{\cdot}CH_3 \rightarrow C_6H_3Cl_2{\cdot}COOH$ (dichlorbenzoic acid)

When substitution is made in the side chain, the only product obtained on oxidation is benzoic acid. Thus,

$$C_6H_5{\cdot}CH_2Cl \rightarrow C_6H_5COOH$$
$$C_6H_5{\cdot}CHCl_2 \rightarrow C_6H_5COOH$$
$$C_6H_5{\cdot}CCl_3 \rightarrow C_6H_5COOH$$

Another method of distinguishing between the members of these two classes of derivatives is found in the action of the halogen atoms. The halogen atoms contained in the side chain act like the halogen atoms in the paraffin derivatives, and those contained in the benzene nucleus do not. For example, if the compound *benzal chloride*, $C_6H_5{\cdot}CHCl_2$, is heated with water under pressure, one atom of oxygen replaces the two atoms of chlorine, forming *benzaldehyde*, $C_6H_5{\cdot}CHO$, or *oil of bitter almonds*. When the isomeric derivative dichlortoluene, $C_6H_3Cl_2{\cdot}CH_3$, is treated in the same manner, no change occurs.

54. The monohalogen substitution products of toluene, such as monochlortoluene are disubstitution products of benzene and as such are capable of existing in three isomeric varieties, ortho, meta, and para. The direct treatment of toluene with chlorine or bromine forms a mixture of the para and ortho compounds. In order to determine to which of these modifications the product belongs, the halogen is replaced by methyl, forming the corresponding xylene.

Xylene forms halogen disubstitution derivatives of the para modification very easily. The other two modifications form monosubstitution products which are separated into their constituents only with great difficulty.

SULPHURIC AND SULPHUROUS ACID DERIVATIVES

SULPHONIC ACIDS

55. Preparation.—The sulphonic acids of the aromatic hydrocarbons are produced by the long-continued action of ordinary hot concentrated sulphuric acid on the hydrocarbon, especially in the case of benzene, or by simply treating the hydrocarbon with fuming sulphuric acid.

56. Properties.—The sulphonic acids are in many cases easily soluble in water and hence are difficultly crystallizable. They are usually separated from their aqueous solutions in the form of their sodium salts by salting out with sodium chloride. This solubility of the sulphonic acids, together with their ease of production, finds an important technical use in the conversion of insoluble aromatic dyes into their sulphonic acid derivatives, which are readily soluble in water.

Most of the salts of the sulphonic acids crystallize well and are used in the purification of the sulphonic acids. Boiling with aqueous solutions of the alkalies does not decompose the sulphonic acids, but fusion with the caustic alkalies forms phenols; thus,

$$C_6H_5{\cdot}SO_3H + KOH = C_6H_5{\cdot}OH + KHSO_3$$

57. Reactions of Sulphonic Acids.—The sulphonic acids are important because they are easily prepared and because they can be used as a starting point in the preparation of numerous other derivatives. The most important reactions into which they enter are illustrated by the following equations:

1. Formation of salts:

$$2C_6H_5SO_2{\cdot}OH+K_2CO_3=2C_6H_5SO_2{\cdot}OK+CO_2+H_2O$$

potassium
benzene sulphonate

2. Phenols:

$$C_6H_5SO_2{\cdot}OH+KOH=C_6H_5OH+KHSO_3$$

phenol or
phenyl hydroxide

3. Cyanides:

$$C_6H_5SO_2{\cdot}OH+KCN=C_6H_5CN+KHSO_3$$

phenyl cyanide

4. Sulphonic chlorides:

$$C_6H_5SO_2{\cdot}OH+PCl_5=C_6H_5SO_2{\cdot}Cl+POCl_3+HCl$$

benzene sulphonic
chloride

5. Sulphonic amides:

$$C_6H_5SO_2{\cdot}Cl+NH_3=C_6H_5SO_2{\cdot}NH_2+HCl$$

benzene sulphonic
amide

6. Esters:

$$C_2H_5OH+C_6H_5SO_2{\cdot}OH=C_6H_5SO_2{\cdot}OC_2H_5+H_2O$$
$$C_2H_5OH+C_6H_5SO_2{\cdot}Cl=C_6H_5SO_2{\cdot}OC_2H_5+HCl$$

ethyl benzene
sulphonate

7. Hydrolysis:

$$C_6H_5SO_2{\cdot}OH+H_2O=C_6H_6+H_2SO_4$$

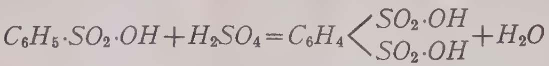
benzene

58. Benzene Monosulphonic Acid, $C_6H_5{\cdot}SO_2{\cdot}OH$.—As already stated, when benzene is treated with sulphuric acid under certain conditions, benzene monosulphonic acid is formed. Thus,

$$C_6H_6+H_2SO_4=C_6H_5{\cdot}SO_2{\cdot}OH+H_2O$$

Benzene monosulphonic acid crystallizes in colorless plates and melts at 50° C. It is very easily soluble in water, is a strong acid, and forms salts and other derivatives.

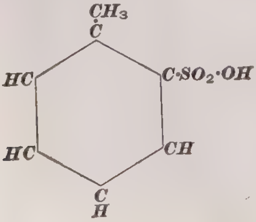
59. Benzene Disulphonic Acid, $C_6H_4(SO_2{\cdot}OH)_2$.—When benzene monosulphonic acid is treated with fuming sulphuric acid, benzene disulphonic acid is formed. Thus,

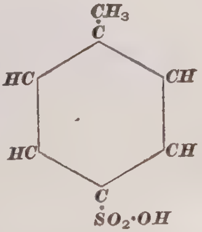


$$C_6H_5{\cdot}SO_2{\cdot}OH + H_2SO_4 = C_6H_4{<}\begin{matrix} SO_2{\cdot}OH \\ SO_2{\cdot}OH \end{matrix} + H_2O$$

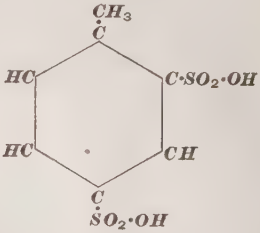
The principal products obtained as the result of the reaction are the meta and para derivatives, with the meta predominating. On prolonged heating, however, the latter passes into the para variety.

60. Sulphonic Acids of Toluene.—The sulphonic acids of toluene and other benzene homologues are prepared by the methods used for the preparation of the benzene sulphonic acids. The reaction between the hydrocarbon and sulphuric acid takes place much more readily, however, because of the presence of the aliphatic radical or side chain. In the case of toluene the sulphonic acid group is substituted in the ortho and para positions. Thus,





If a second sulphonic acid group is introduced, it enters the ring at a position that is meta to the first group. Thus,



The sulphonic acids of toluene are of two classes, as were the halogen substitution products. When the sulphonic acid group enters the nucleus, a true aromatic sulphonic acid results, and when it is substituted in the side chain, as in benzyl sulphonic acid, $C_6H_5 \cdot CH_2 \cdot SO_2 \cdot OH$, the compound obtained is essentially an aliphatic sulphonic acid.

SULPHINIC ACIDS

61. The sulphurous acid derivatives of the aromatic hydrocarbons are known as *sulphinic acids*. They are not formed by the action of sulphurous acid on the hydrocarbon but result from the reduction of sulphonic acids and sulphonic chlorides or by the treatment of the hydrocarbon with sulphur dioxide, SO_2. Thus,

$$C_6H_6 + SO_2 = C_6H_5 \cdot SO_2H$$

The sulphinic acids are of theoretical importance only.

NITRIC AND NITROUS ACID DERIVATIVES

NITRO COMPOUNDS

62. Formation and Properties.—A characteristic difference between the aliphatic and aromatic hydrocarbons is the ease with which the latter are converted into nitro derivatives by the action of concentrated nitric acid. The method employed in the preparation of the nitro compounds of the aromatic series is to treat the hydrocarbon with a mixture of nitric and sulphuric acids or with fuming nitric acid. Without the presence of the sulphuric acid, however, the water formed in the process of nitration would so dilute the nitric acid that its action would be retarded. An increase in the number of alkyl groups attached to the benzene nucleus affords a corresponding increase in the ease of nitration. While all the hydrogen in benzene may be readily replaced by a halogen, it is different in regard to the introduction of the nitro group. Very little trouble is experienced in introducing the first two nitro groups, but the introduction of the third can be effected only with difficulty.

The nitro compounds are neither acids nor esters of nitrous acid. That they are not esters is shown by the fact that they do not yield a nitrite and hydroxyl derivatives as do esters on saponification with caustic potash. Since the nitrogen of the nitro compounds is linked to a tertiary carbon atom, they do not contain hydrogen replaceable by metals. Nascent hydrogen reduces the nitro compounds to amino compounds.

63. Mononitrobenzene, $C_6H_5NO_2$.—Mononitrobenzene is prepared by slowly pouring a cold mixture consisting of about 60 per cent. of concentrated sulphuric acid and 40 per cent. of concentrated nitric acid into benzene. During the addition of the mixed acids the contents of the reaction vessel must be well stirred and the temperature of the reaction mixture must not be allowed to rise above 25° C. When all of the acid has been added and the temperature remains stationary or begins to fall, the reaction mixture is heated to between 50° and 60° C., for about an hour in a flask equipped with a reflux condenser. The contents of the flask are then cooled, and as the nitrobenzene is lighter than the acid, two liquid layers are formed and a separation may be effected by means of a separatory funnel. The nitrobenzene is then washed with water, then with a dilute solution of sodium carbonate, and finally with water. It is then dried over anhydrous calcium chloride and distilled. If distilled with steam, drying may be dispensed with at this point.

64. Nitrobenzene is a colorless, or faintly yellowish, oily liquid with an odor and taste resembling that of bitter almonds, and hence is used in perfumery instead of the essential oil of bitter almonds. It is known as *oil of mirbane.* It has a specific gravity of 1.2 at 25° C., boils at 209° C., and is soluble in alcohol, ether, and oils. Its principal use is in the manufacture of aniline by its reduction; thus,

$$C_6H_5NO_2+3H_2=C_6H_5NH_2+2H_2O$$

65. Dinitrobenzenes, $C_6H_4(NO_2)_2$.—Dinitrobenzene is formed in the three isomeric modifications 1–2 dinitrobenzene, 1–3 dinitrobenzene, and 1–4 dinitrobenzene. The three modifications are formed by nitrating benzene with sulphuric acid and fuming nitric acid and boiling the mixture. In this formation the meta modification is formed in greatest quantity and on crystallizing the mixture from alcohol it separates out first, the ortho- and para-dinitrobenzenes remaining in solution.

Meta-dinitrobenzene forms yellowish, crystalline needles soluble in alcohol. They melt at 90° C. and boil at 297° C. Nascent hydrogen reduces it to meta-phenylenediamine, $C_6H_4(NH_2)_2$, a solid compound, soluble in water, alcohol and ether, having a melting point at 63° C. and boiling at 283° C. Strong nitration with a mixture of nitric acid and fuming sulphuric acid converts meta-dinitrobenzene into *symmetrical trinitrobenzene* (1–3–5), which melts at 121° C.

Ortho-dinitrobenzene and *para-dinitrobenzene* are colorless, crystalline substances melting at 116° C. and 172° C., respectively. Heating the dinitrobenzenes with chlorine or bromine to 200° C., wholly replaces the nitro groups by halogens.

66. Nitrotoluenes.—When toluene is subjected to nitration the nitro group always enters the nucleus, and the reaction produces *mononitrotoluenes*, $C_6H_4(NO_2) \cdot CH_3$. The chief products of nitration are the ortho and the para compounds; the meta compound is formed only in small quantities. *Ortho-nitrotoluene* (1–2) is a yellowish liquid with a specific gravity of 1.168, and boils at 218° C. It is soluble in alcohol, ether, and petroleum ether. *Meta-nitrotoluene* (1–3) forms yellowish crystals melting at 16° C. and boiling at 230° C. It has a specific gravity of 1.164, and is soluble in alcohol and ether. *Para-nitrotoluene* (1–4) also forms yellowish crystals, which melt at 54° C. and boil at 236° C. Its solubilities are the same as those of the meta compound. Reduction of the nitrotoluenes converts them into the corresponding amino compounds.

Dinitrotoluene, $C_6H_3(NO_2)_2 \cdot CH_3$ (1–2–4), is formed either by the further nitration of ortho- and para-nitrotoluene or by treating toluene with an excess of a mixture of nitric and sulphuric acids. It is a yellow, crystalline substance melting at

70° C., and is soluble in hot alcohol. Another dinitrotoluene (1–2–5) melting at 48° C. is formed at the same time as the 1–2–4 modification.

67. Trinitrotoluene, $C_6H_2(NO_3)_3 \cdot CH_3$.—Trinitrotoluene may be prepared by treating toluene with a mixture of sulphuric and fuming nitric acids. On a commercial scale it is usual to conduct the nitration in three stages. Thus, the mononitro derivative is first formed and separated, then the dinitro derivative from this, and finally trinitrotoluene by further nitration of the dinitro derivative. Trinitrotoluene is the military explosive commonly known as T. N. T. It is regarded as a "safe" explosive and extreme care is not necessary in handling it. Thus, the pure compound may be heated or brought in contact with a flame without causing an explosion. It is not sensitive to ordinary shock and is usually detonated, or caused to explode, by means of mercury fulminate. Trinitrotoluene is soluble in alcohol. It forms crystals that melt at 80° C.

NITROSO COMPOUNDS

68. Nitrosobenzene, C_6H_5NO.—Although nitrosobenzene is regarded as the nitrous acid derivative of benzene, it cannot be obtained by the action of the acid on the hydrocarbon. It may be prepared indirectly by the oxidation of phenylhydroxylamine, $C_6H_5NH \cdot OH$. The latter is formed when nitrobenzene is partly reduced by means of zinc dust in a neutral solution, such as hot dilute alcohol or hot water. Thus,

$$C_6H_5NO_2 + 2H_2 = C_6H_5NH \cdot OH + H_2O$$
$$C_6H_5NH \cdot OH + O = C_6H_5NO + H_2O$$

Nitrosobenzene is a yellow, crystalline compound that melts at 68° C. It is soluble in alcohol, ether, and chloroform. When heated above its melting point it is converted into an emerald green liquid.

Other nitroso derivatives are known, which will subsequently be treated as such in connection with the compounds from which they are derived.

AMINO DERIVATIVES

GENERAL PREPARATION AND PROPERTIES

69. Preparation.—The amino derivatives of the benzene series form two distinct classes of compounds, one in which the NH_2 group is attached to the nucelus and the other in which the group is attached to the side chain. The derivatives of the first class are made almost exclusively by the action of nascent hydrogen on the corresponding nitro compound. This is effected by means of the action of hydrochloric acid on tin, or by the action of either hydrochloric acid or acetic acid on iron filings. On a manufacturing scale, iron filings and hydrochloric acid are usually employed. Several of these derivatives are well known, the simplest and best known being aminobenzene, or aniline.

70. Properties.—The aromatic amino compounds, when pure, are colorless liquids or white opaque solids that possess a characteristic odor. They are only slightly soluble in water but are very soluble in alcohol and ether. The amino compounds may be distilled directly without decomposition. They may also be distilled with steam. Because of their basic nature they form salts with acids. These salts are soluble in water.

71. Aniline, $C_6H_5NH_2$.—Aniline, also known as aminobenzene and phenylamine, was discovered in 1826 by Unverdorben, among the products resulting from the distillation of indigo. The name aniline is derived from the Spanish word *anil* for indigo. Aniline is also found in small quantities in coal tar and in bone oil. It may be prepared in the laboratory by the action of hydrochloric acid and tin on nitrobenzene. In the experiment, 50 grams of nitrobenzene and 90 grams of granulated tin are placed in a round-bottom, 1-liter flask with a stopper through which passes the end of a reflux condenser and the stem of a dropping funnel. The contents of the flask are gently heated on a water bath and 200 cubic centimeters of concentrated hydrochloric acid are slowly added through the dropping funnel, from time to time, the flask and contents being shaken after each addition. A vigorous reaction takes place, and if it becomes too violent, the flask should be cooled by immersion in cold water. When all of the acid has been added, heating is continued for about an hour; then the reaction mixture is allowed to cool until crystallization begins. The condenser and funnel are removed and a strong solution of caustic soda is slowly added until the precipitate at first formed is dissolved. The contents of the flask are then distilled with steam. Two layers, the upper of aniline and the lower of water, will form in the receiver and a separation is effected by means of a separatory funnel. The aniline thus obtained is redistilled over a flame. The cloudy distillate, which contains some water, and passes over first, is discarded; and the remainder, which boils at 182° C., is collected.

In the foregoing method, a salt of aniline is first formed. Thus,

$$2C_6H_5NO_2+3Sn+14HCl=\underset{\substack{\text{aniline}\\\text{hydrochloride}}}{2C_6H_5NH_2\cdot HCl}+3SnCl_4+4H_2O$$

The aniline is then set free by means of caustic soda. Thus,

$$C_6H_5NH_2\cdot HCl+NaOH=C_6H_5NH_2+NaCl+H_2O$$

72. Aniline is prepared on a large scale by a method similar to that just given. Reduction of the nitrobenzene is effected, however, by means of iron filings and hydrochloric acid for the sake of economy and efficiency. The reaction that takes place may be represented theoretically as follows:

$$C_6H_5NO_2+3Fe+6HCl=C_6H_5NH_2+3FeCl_2+2H_2O$$

In making use of this reaction, one fact is noticed, namely, that only about one-fortieth of the hydrochloric acid required by the equation is needed for the reduction. This is due to the fact that iron filings and water in the presence of ferrous chloride are able to effect the reduction.

$$C_6H_5NO_2+2Fe+4H_2O=C_6H_5NH_2+2Fe(OH)_3$$

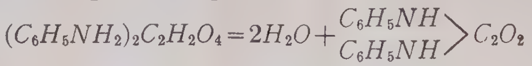
In this process all of the acid reacts with iron to form ferrous chloride. Consequently, none remains to form aniline hydrochloride and the aniline is at once obtained in the free state. This makes for economy, since the use of caustic soda is unnecessary. The industrial process just described may also be used in the laboratory preparation of aniline.

73. Properties of Aniline.—Pure aniline is a colorless liquid that soon becomes dark in color on exposure to air, due to slight oxidation. It is soluble in water to the extent of about 3 per cent., but is easily soluble in alcohol, ether, acetone, and oils. It has a specific gravity of 1.0214 at 25° C., melts at $-8°$ C., and boils at 182.5° C. Although aniline has only feeble basic properties, it will precipitate zinc, aluminum, and ferric salts. It is poisonous.

Aniline bears the same relation to benzene that aminoethane bears to ethane. As it is a substituted ammonia, it unites directly with acids, forming salts. Addition of acids to aniline forms various colored salts that have great brilliancy and are used in the arts. Thus, if a nitrate and sulphuric acid are added to aniline, a red color is produced. Aniline is also used in the manufacture of various medicinal compounds.

74. Salts of Aniline.—Aniline is considerably more sensitive to the action of oxidizing agents and to reagents in general than is benzene or the halogen or nitro derivatives of benzene. Substitution is easily effected, but there is danger that the substituting agent will decompose the aniline. By treating aniline with acids, salts are formed direct. Thus, with hydrochloric acid, *aniline hydrochloride*, $C_6H_5NH_2{\cdot}HCl$, is obtained. This is known commercially as *aniline salt*, and is an almost colorless crystalline substance that is freely soluble in water and alcohol and melts at 192° C. *Aniline nitrate*, $C_6H_5NH_2{\cdot}HNO_3$, crystallizes in large, colorless to yellowish rhombic plates, is soluble in water and alcohol, and decomposes at 190° C. *Aniline oxalate*, $(C_6H_5NH_2)_2C_2H_2O_4$, crystallizes from its aqueous solution in large, white rhombic prisms.

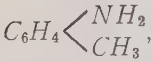
When exposed to heat, water is driven off and *oxanilide* is formed according to the equation



$$(C_6H_5NH_2)_2C_2H_2O_4 = 2H_2O + \begin{matrix} C_6H_5NH \\ C_6H_5NH \end{matrix}\!\!>C_2O_2$$

75. Anhydroformaldehydeaniline, $(C_6H_5N{:}CH_2)_3$.—Aniline reacts with formaldehyde to form anhydroformaldehydeaniline, a condensation product. It melts at 40° C., and the reaction by which it is formed is used for the identification of both aniline and formaldehyde. Of special interest is its reaction with nascent hydrogen to form the secondary amine, methyl aniline.

AMINOTOLUENES

76. Preparation and Properties.—The aminotoluenes,  $C_6H_4\!\!<\!\begin{matrix} NH_2 \\ CH_3 \end{matrix}$, or *toluidines*, of which there are three, are prepared by the reduction of the corresponding nitrotoluenes. As para-nitrotoluene is the best known of the nitrotoluenes, so para-toluidine is the best known of the three toluidines. *Ortho-toluidine* is a colorless liquid boiling at 199.7° C. and having a specific gravity of 1.003. Exposed to the air, it acquires a pink color. It is crystallizable, yielding reddish crystals, and is soluble in water and alcohol. *Meta-toluidine* is a reddish-brown liquid having a specific gravity of .998 and boiling at 203° C. It is soluble in alcohol and ether. *Para-toluidine* is a solid crystallizing from its alcohol solution in white, lustrous plates having a peculiar odor. It is soluble in alcohol and ether, melts at 45° C., and boils at 200° C.

The properties of the toluidines resemble very closely those of aniline. A mixture of the toluidines and aniline treated with oxidizing agents is converted into *rosaniline*, the mother substance of the aniline dyes.

77. Benzylamine, $C_6H_5{\cdot}CH_2{\cdot}NH_2$.—The amino derivatives that have been described, belong to that class in which the amino group has been substituted in the nucleus. In that class represented by benzylamine, and which is of much less importance than the first class, the amino group is substituted in the side chain. Amines of this type have chemical properties similar to those of the aliphatic amines. Benzylamine is obtained by the methods employed for the preparation of the aliphatic amines. Thus, it is formed when benzyl chloride is heated with ammonia,

$$C_6H_5{\cdot}CH_2{\cdot}Cl+NH_3=C_6H_5{\cdot}CH_2{\cdot}NH_2+HCl$$

It is also produced by the reduction of phenyl cyanide,

$$C_6H_5CN+4H=C_6H_5{\cdot}CH_2{\cdot}NH_2$$

Benzylamine is a colorless, limpid liquid with a strongly alkaline reaction. It has a specific gravity of .99, is soluble in all proportions of water and alcohol, and boils at 184° C. It is volatile with steam.

DERIVATIVES OF AROMATIC AMINES

ANILIDES

78. General Preparation and Properties.—Aniline and its homologues form derivatives with fatty acids known as *anilides*. These compounds are acid amides in which an amino-hydrogen atom has been replaced by a phenyl group. They are prepared by heating the aniline salts of the fatty acids. They are prepared also by the action of aniline on the acid chlorides according to the equation

$$C_6H_5NH_2+CH_3{\cdot}COCl=C_6H_5NH{\cdot}CO{\cdot}CH_3+HCl$$

and by treating aniline with the acid anhydrides.

The acid anilides are very stable and can usually be distilled without decomposition. They can also be readily chlorinated and nitrated. They are resolved into their component parts by digestion with alkalies or by heating with hydrochloric acid, and form a rapid and simple means of distinguishing the aromatic bases.

Thus, although it is impossible to effect a separation of the toluidines by fractional distillation because of the closeness of their boiling points, it may be accomplished by taking advantage of the great differences in the melting points of their acetyl derivatives. The boiling points of the toluidines, together with the melting points of the corresponding acetotoluides, are given for the sake of comparison:

	Boiling Point Degrees C.		Melting Point Degrees C.
Ortho-toluidine	199.7	Ortho-acetotoluide	110
Meta-toluidine	203.0	Meta-acetotoluide	63
Para-toluidine	200.0	Para-acetotoluide	153

79. Acetanilide, $C_6H_5NH \cdot CO \cdot CH_3$.—Acetanilide may be prepared by boiling aniline for several hours with an excess of glacial acetic acid. The flask used is provided with a reflux condenser, which in the present case may consist merely of an air-cooled glass tube about 1 centimeter in diameter and about 50 centimeters in length. Aniline acetate is first formed; but, as the heating is continued, it loses water and is converted into acetanilide. The reactions that take place may be represented as follows:

$$C_6H_5NH_2 + CH_3COOH = C_6H_5NH_2 \cdot CH_3COOH$$
$$C_6H_5NH_2 \cdot CH_3COOH = C_6H_5NH \cdot CO \cdot CH_3 + H_2O$$

When the reaction is complete, say after 10 hours of boiling, the contents of the flask are poured into hot water containing a small quantity of hydrochloric acid. On cooling, the acetanilide crystallizes and may be purified by recrystallization from water. Acetanilide is sparingly soluble in cold water but dissolves easily in hot water. It crystallizes from water in the form of shining plates that melt at 114° C. It boils at 305° C. Acetanilide is used in medicine as a febrifuge, or fever reducer, under the name of *antifebrin*.

The anilides of other organic acids, such as formic and oxalic acids, may be prepared by the method described for acetanilide.

ALKYL AND ARYL AMINES

80. Classification.—As in the case of the aliphatic amines, the hydrogen of the NH_2 group of the aromatic primary amines may be replaced by *alkyl* or aliphatic radicals and *aryl* or aromatic radicals. This fact gives rise to three classes of amino compounds, primary, secondary, and tertiary. In what follows, they are represented by aniline and the derivatives obtained by substituting either an alkyl or an aryl radical for the hydrogen of the amino group. The compounds that will be used for the purpose of illustrating methods of preparation and properties common to this class of compounds are:

Primary	Secondary	Tertiary
$C_6H_5NH_2$ aniline	$C_6H_5NH\cdot CH_3$ monomethylaniline	$C_6H_5N\cdot(CH_3)_2$ dimethylaniline
	$C_6H_5NH\cdot C_6H_5$ diphenylamine	$C_6H_5N\cdot(C_6H_5)_2$ triphenylamine

81. Monomethylaniline, $C_6H_5NH\cdot CH_3$.—Monomethylaniline is prepared by many methods, most of which involve heating an excess of aniline with methyl alcohol under pressure in the presence of a halogen, or heating the alcohol and the halogen acid with aniline under a reflux condenser. In another method, a salt of aniline, such as the hydrochloride, is heated with the alcohol. In order that the maximum yield of monomethyl aniline may be realized, it is necessary that the aniline be in excess of that required by theory. The reactions that take place when the foregoing methods are used, may be represented as follows:

In the presence of a halogen or the halogen acid:

$$C_6H_5NH_2+CH_3OH=C_6H_5NH\cdot CH_3+H_2O$$

Using a salt of aniline:

$$C_6H_5NH_2\cdot HCl+CH_3OH=C_6H_5NH\cdot CH_3+HCl+H_2O$$

The methyl aniline obtained by any of these methods is not pure but contains some dimethylaniline from which it may be separated by a method that will subsequently be described.

Monomethylaniline of a high degree of purity may be prepared by a method based on the reaction that takes place between anhydroformaldehydeaniline, $(C_6H_5N:CH_2)_3$ and nascent hydrogen. Thus,

$$(C_6H_5N:CH_2)_3+6H=3C_6H_5NH\cdot CH_3$$

The reaction is brought about by heating a vigorously agitated mixture of aniline, water, and zinc dust to the boiling point and then slowly introducing at two points beneath the level of the mixture, formaldehyde and a 25 per cent. solution of caustic soda. The product obtained is separated from the accompanying water as completely as possible and is then distilled.

82. Another method for the preparation of monomethylaniline, which is of theoretical interest, consists in replacing the amino hydrogen of acetanilide by sodium, methylating the sodium acetanilide formed and then saponifying the product. The reactions may be carried out by heating a solution of acetanilide in xylene with metallic sodium, sodium acetanilide being formed. Thus,

$$C_6H_5NH \cdot CO \cdot CH_3 + Na = C_6H_5NNa \cdot CO \cdot CH_3 + H$$

When sodium acetanilide is methylated by treatment with methyl iodide, methylacetanilide is formed.

$$C_6H_5NNa \cdot CO \cdot CH_3 + CH_3I = C_6H_5N \cdot CH_3CO \cdot CH_3 + NaI$$

On saponifying the methylacetanilide, monomethylaniline is set free.

$$C_6H_5N \cdot CH_3CO \cdot CH_3 + H_2O = C_6H_5NH \cdot CH_3 + CH_3COOH$$

Monomethylaniline, when pure, is a colorless liquid that boils at 193° C. and has a specific gravity of .9855 at 25° C. It is only slightly soluble in water but is easily dissolved by alcohol or ether. It darkens on exposure to air and has an odor resembling that of aniline.

83. Dimethylaniline, $C_6H_5N(CH_3)_2$.—Dimethylaniline is the most important member of that class of compounds known as mixed tertiary amines. It is prepared from methyl alcohol and a salt of aniline, as is monomethylaniline. In fact, by the methods described for the preparation of monomethylaniline, in which aniline, methyl alcohol, and a halogen are used, it is impossible to prevent the formation of dimethylaniline. In the preparation of the latter the reaction is controlled to a certain extent by using an excess of alcohol. In this way the maximum yield of dimethylaniline is obtained. The reactions may be represented as follows:

$$C_6H_5NH_2 \cdot HCl + 2CH_3OH = C_6H_5N(CH_3)_2 \cdot HCl + 2H_2O$$
$$C_6H_5N(CH_3)_2 \cdot HCl + NaOH = C_6H_5N(CH_3)_2 + NaCl + H_2O$$

A separation of aniline, monomethylaniline and dimethylaniline is effected in the laboratory by treating the mixture with acetic anhydride, thus converting the primary and secondary amines into their acetyl derivatives, which are not formed by tertiary amines since they do not contain amino hydrogen. Thus,

$$2C_6H_5NH_2 + (CH_3CO)_2O = 2\underset{\text{acetanilide}}{C_6H_5NH \cdot CO \cdot CH_3} + H_2O$$
$$2C_6H_5NH \cdot CH_3 + (CH_3CO)_2O = 2\underset{\text{methylacetanilide}}{C_6H_5N \cdot CH_3CO \cdot CH_3} + H_2O$$

Acetanilide boils at 305° C., and methylacetanilide at 253° C., under a pressure of 712 millimeters; and since the boiling point of dimethylaniline is 193° C., it can easily be separated by fractional distillation.

Dimethylaniline is an oily liquid that is colorless when pure but that darkens on exposure to air. It boils at 193° C. and has a specific gravity of .954 at 25° C. It is insoluble in water, but dissolves readily in alcohol or ether.

84. Diphenylamine, $C_6H_5NH \cdot C_6H_5$.—Diphenylamine is a type of the true secondary aromatic amines. It is formed from aniline by the substitution of a phenyl group for one of the ammonia hydrogen atoms. It is used on a large scale in the manufacture of dyes. It is best prepared by heating aniline with aniline hydrochloride at 240° C.; thus,

$$C_6H_5NH_2 + C_6H_5NH_2 \cdot HCl = C_6H_5NH \cdot C_6H_5 + NH_4Cl$$

Diphenylamine crystallizes in white leaflets that melt at 54° C. and boil at 310° C. It is soluble in acids and alcohol but only slightly soluble in water. It readily forms salts with strong acids, but these are decomposed by water. Diphenylamine has an agreeable floral odor. It is a very sensitive reagent for the detection of nitric acid, which produces a deep blue color with its solution in concentrated sulphuric acid.

This test cannot be used in the presence of other oxidizing agents, such as bromine water or permanganate.

85. Triphenylamine, $(C_6H_5)_3N$.—Triphenylamine is one of the few, true, aromatic, tertiary amines that are known. It may be prepared by the action of metallic sodium and brom-benzene on diphenylamine. Sodium diphenylamine is first formed,

$$(C_6H_5)_2NH+Na=(C_6H_5)_2NNa+H$$

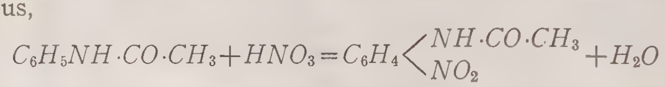
which in turn is acted on by the brombenzene to form triphenylamine,

$$(C_6H_5)_2NNa+C_6H_5Br=(C_6H_5)_3N+NaBr$$

Triphenylamine crystallizes from ether in large prisms that melt at 127° C. It distills without decomposition at 347° C. It is soluble in benzene, acetone, and hot alcohol, but sparingly soluble in cold alcohol. Triphenylamine does not have a basic character, and consequently cannot form salts with acids. It dissolves in sulphuric acid, forming first a violet and then a dark-green color.

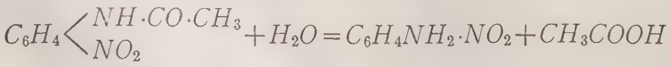
SUBSTITUTED ANILINES

86. Nitranilines, $C_6H_4\Big<\begin{matrix}NH_2\\NO_2\end{matrix}$.—The nitranilines may be prepared by the action of cold, fuming nitric acid on acetanilide. Thus,



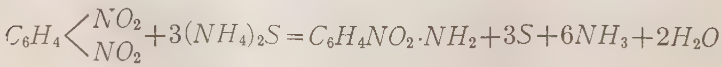
$$C_6H_5NH\cdot CO\cdot CH_3+HNO_3=C_6H_4\Big<\begin{matrix}NH\cdot CO\cdot CH_3\\NO_2\end{matrix}+H_2O$$

The ortho- and para-nitracetanilides thus formed are precipitated by the addition of water, filtered, and then washed. They may be separated by taking advantage of the solubility of the ortho compound in chloroform. The corresponding nitranilines are then obtained by hydrolysis. Thus,



$$C_6H_4\Big<\begin{matrix}NH\cdot CO\cdot CH_3\\NO_2\end{matrix}+H_2O=C_6H_4NH_2\cdot NO_2+CH_3COOH$$

Meta-nitraniline is readily prepared by partly reducing meta-dinitrobenzene with ammonium sulphide in alcoholic solution. Thus,

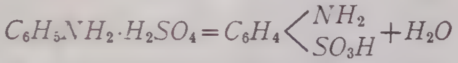


$$C_6H_4\Big<\begin{matrix}NO_2\\NO_2\end{matrix}+3(NH_4)_2S=C_6H_4NO_2\cdot NH_2+3S+6NH_3+2H_2O$$

Ortho-nitraniline melts at 70° C., meta-nitraniline at 112° C., and para-nitraniline at 148° C. They are only slightly soluble in water, but readily dissolve in alcohol and in ether.

87. Sulphanilic Acid, $C_6H_4\Big\langle{}^{NH_2}_{SO_3H}$.—Sulphanilic acid is formed when aniline is heated with concentrated or fuming sulphuric acid. Aniline acid sulphate is first formed, which, however, loses water on heating, with the formation of sulphanilic acid. Thus,

$$C_6H_5NH_2+H_2SO_4=C_6H_5NH_2\cdot H_2SO_4$$



$$C_6H_5NH_2\cdot H_2SO_4=C_6H_4\Big\langle{}^{NH_2}_{SO_3H}+H_2O$$

The product thus obtained is cooled, washed with cold water, filtered, and then purified by crystallization from boiling water. Sulphanilic acid is a colorless, crystalline solid only slightly soluble in water, and insoluble in alcohol and ether. It crystallizes from hot water in rhombic plates containing one molecule of water. These are efflorescent in the air. Sulphanilic acid does not melt, but chars at temperatures above 280° C. The introduction of the sulphonic acid group weakens the basic properties of aniline, and consequently sulphanilic acid does not yield salts with acids.

DIAZO COMPOUNDS AND THEIR DERIVATIVES

DIAZO COMPOUNDS

88. Diazotization.—By diazotization is meant that process of treating an amino compound or its salt with nitrous acid in the cold, with the resultant formation of a diazo or diazonium compound. The simpler reactions with nitrous acid are illustrated by means of aniline and its salts. Thus,

$$C_6H_5NH_2+HNO_2=\underbrace{C_6H_5N_2\cdot OH}_{\substack{\text{diazo benzene or}\\ \text{benzene diazonium hydroxide}}}+H_2O$$

If a salt of an amine, such as the hydrochloride, nitrate, or sulphate of aniline, is treated in the same manner, a salt of the diazo compound is obtained. Thus,

$$C_6H_5NH_2 \cdot HCl + HNO_2 = C_6H_5N_2 \cdot Cl + 2H_2O$$

diazo benzene chloride or
benzene diazonium chloride

$$C_6H_5NH_2 \cdot HNO_3 + HNO_2 = C_6H_5N_2 \cdot NO_3 + 2H_2O$$

diazo benzene nitrate or
benzene diazonium nitrate

$$C_6H_5NH_2 \cdot H_2SO_4 + HNO_2 = C_6H_5N_2 \cdot HSO_4 + 2H_2O$$

diazo benzene sulphate or
benzene diazonium sulphate

89. General Laboratory Method.—The diazotization of the salt of an amine in aqueous solution, when it is not desired to isolate the diazonium compound, may be carried out as follows by using proportionate quantities of the compounds indicated: One molecule (a gram-molecule or the molecular weight in grams), of the amine is dissolved in about 15 parts of water that contains about 3 molecules of hydrochloric acid or other mineral acid. Ice is then added to the solution, the temperature of which is brought down to and maintained at about 5° C. by the further addition of ice, as the temperature of the reaction mixture tends to rise on the addition of sodium nitrite solution, 1 molecule of which is slowly introduced with constant stirring. The reactions that take place are represented by the following equations:

$$C_6H_5NH_2 + HCl = C_6H_5NH_2 \cdot HCl$$
$$NaNO_2 + HCl = NaCl + HNO_2$$
$$C_6H_5NH_2 \cdot HCl + HNO_2 = C_6H_5N_2 \cdot Cl + 2H_2O$$

When all of the sodium nitrite solution has been introduced, the stirring is continued for about 10 minutes and the solution tested with a strip of filter paper that has been treated with potassium iodide and starch. If free nitrous acid is present, it will of course be indicated by the formation of a blue color on the paper. Only a faint acid reaction is desirable, and if the starch-iodide paper indicates the presence of a large excess of nitrous acid, additional quantities of the amine are introduced. If there is no free nitrous acid present, however, sodium nitrite solution is added to slight excess. When these operations are carried out carefully, practically all of the amine will be converted to the diazonium salt.

90. If, for the purpose of studying the properties of the diazonium salts, it is necessary to isolate them, diazotization is carried out by adding amyl nitrite to the cold alcoholic solution of the amine to which the necessary quantity of acid has also been added. The reaction may be represented by the equation

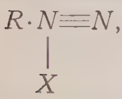
$$C_6H_5NH_2{\cdot}HCl+C_5H_{11}NO_2=C_6H_5N_2{\cdot}Cl+C_5H_{11}OH+H_2O$$

The diazonium salt crystallizes within a short time and may be purified by washing with alcohol and ether.

91. General Properties of Diazo Compounds.—The diazo compounds are colorless crystalline compounds that in the dry state are very unstable and of an explosive nature. For this reason, and because of the fact that all of their reactions with other compounds occur in solution, they are seldom isolated. When it is necessary to isolate them, only from .1 to .2 gram is ever handled in the dry state. When prepared in the laboratory, the apparatus used should not be allowed to become dry on the conclusion of the work, but should be immediately rinsed out and washed.

Chemically, the diazo compounds are very active, and as the diazo group is very easily replaced, numerous classes of compounds may be readily prepared from them. Primarily, the diazo compounds are of great importance because of their use in the preparation of dyes.

92. Structure of Diazo Compounds.—The exact structure of the diazo compounds is unknown, although several plausible formulas have been developed by prominent investigators, among whom may be mentioned, Kekulé, and Bloomstrand. According to Kekulé, diazo compounds have the general structure $R{\cdot}N{=}N{\cdot}X$, in which R represents an aromatic radical such as C_6H_5, and X a halogen atom, and in which nitrogen is trivalent. Bloomstrand, however, suggests the formula $R{\cdot}N{\equiv}N$, in which one of the nitrogen atoms is pentavalent.



$$R{\cdot}\underset{\substack{|\\ X}}{N}{\equiv}N$$

Each of the formulas accounts for some of the properties of the diazo compounds, but neither of them accounts for all of their properties. Therefore, it is evident that the diazo compounds furnish an example of a peculiar form of isomerism. In the case of isomeric compounds, one formula is used to represent different compounds of the same molecular weight that differ from one another in their structures and properties. In the case of the diazo compounds, however, two formulas are required to account for all of the properties of one compound. The phenomenon exhibited by a compound of this type is designated as *tautomerism.*

REACTIONS OF DIAZO COMPOUNDS

93. Reduction.—When the diazo compounds are subjected to the action of reducing agents, the corresponding hydrocarbon is obtained; thus,

$$C_6H_5N_2\cdot Cl + H_2 = C_6H_6 + HCl + N_2$$

On boiling with alcohol, the diazonium compound is reduced to the hydrocarbon and the alcohol is oxidized to aldehyde. Thus,

$$C_6H_5N_2\cdot Cl + C_2H_5OH = C_6H_6 + CH_3\cdot CHO + HCl + N_2$$

Reduction to the hydrocarbon also results when stannous chloride is employed.

94. Reaction With Water.—When the aqueous solutions of diazonium compounds are heated, the compounds decompose with the formation of a class of compounds called phenols; thus,

$$C_6H_5N_2\cdot Cl + H_2O = \underset{\substack{\text{phenol or}\\ \text{hydroxy benzene}}}{C_6H_5OH} + HCl + N_2$$

95. Reaction With Halogen Acids.—If the aqueous solution of the diazonium compound is warmed with a halogen acid, the halogen derivative of the corresponding hydrocarbon is obtained; thus,

$$C_6H_5N_2\cdot Cl + HI = C_6H_5I + HCl + N_2$$

The halogen derivative is also obtained when the potassium salt of the halogen acid is employed; thus,

$$C_6H_5N_2\cdot Cl + KI = C_6H_5I + KCl + N_2$$

96. Sandmeyer Reactions.—Sandmeyer discovered that those reactions in which a halogen substitution product of benzene was produced, and other reactions as well, could be made to take place much more readily in the presence of a cuprous salt. The exact mechanism of the reactions that occur is unknown, but the final result may be represented by the following equations:

In the presence of hydrochloric acid and cuprous chloride:

$$C_6H_5N_2 \cdot Cl + 2CuCl = C_6H_5Cl + 2CuCl + N_2$$

In the presence of hydrobromic acid and cuprous bromide:

$$C_6H_5N_2 \cdot Cl + 2CuBr = C_6H_5Br + CuBr + CuCl + N_2$$

In the presence of potassium cyanide and cuprous cyanide:

$$C_6H_5N_2 \cdot Cl + 2CuCN = C_6H_5CN + CuCN + CuCl + N_2$$

In the laboratory, Sandmeyer's reactions are carried out by first forming the diazonium salt, in the usual manner. Its solution is then slowly added with constant stirring to a boiling 10 per cent. solution of the cuprous salt The product is then recovered by steam distillation or by other methods, according to its nature.

97. Diazoamino Compounds.—When a diazo compound acts on an amino compound in the absence of an acid, a diazoamino compound is formed; thus,

$$C_6H_5N_2 \cdot Cl + C_6H_5NH_2 = C_6H_5N{=}N \cdot NH \cdot C_6H_5 + HCl$$

As can be readily seen from the equation, the residue of the diazo salt takes the place of one of the hydrogen atoms of the amino group.

Diazoaminobenzene prepared according to the preceding reaction forms golden-yellow scales soluble in ether and hot alcohol and melting at 96° C. Heated to a high temperature it explodes violently.

AZO COMPOUNDS AND THEIR DERIVATIVES

AZO COMPOUNDS

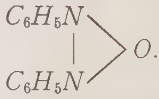
98. Structure and Formation.—The general formula for the azo compounds is represented by the formula $R—N═N—R$, in which each nitrogen atom is linked directly to an aromatic radical. This class of compounds differs, therefore, from the diazo compounds, in that, in the latter, only one of the nitrogen atoms is directly linked to an aromatic radical.

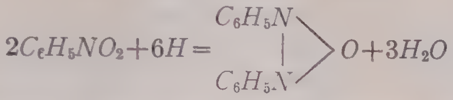
When the nitro group is completely reduced, the resulting compound contains the amino group. The formation of aniline by the reduction of mononitrobenzene is an illustration. However, by varying the conditions under which the reduction takes place, the degree of reduction and the type of compound that will be formed is influenced so that it is possible to obtain a series of compounds, called azo compounds, that occupy a position intermediate between the nitro compounds and the amino compounds. All of the typical reactions that take place in the formation of these derivatives are illustrated by the use of mononitrobenzene.

99. Phenylhydroxylamine, $C_6H_5NH{\cdot}OH$.—It has been shown that aniline is produced when mononitrobenzene is reduced in acid solution. If, however, the reduction of nitrobenzene is carried out in a neutral solution, as, for instance, by the action of zinc dust in alcohol or in hot water, or by means of aluminum amalgam and water, a compound known as phenylhydroxylamine is produced. Thus,

$$C_6H_5NO_2+4H=C_6H_5NH{\cdot}OH+H_2O$$

Phenylhydroxylamine crystallizes in glittering needles that melt at 81° C. It is only slightly soluble in cold water, readily soluble in hot water, and very soluble in alcohol and ether.

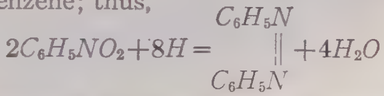
100. Azoxybenzene,  $\left.\begin{array}{l}C_6H_5N\\ \;\;|\\ C_6H_5N\end{array}\right>O$.—Azoxybenzene is produced when nitrobenzene is reduced incompletely in alkaline solution, as by the action of zinc dust and caustic soda or stannous chloride and caustic soda. Thus,



$$2C_6H_5NO_2+6H=\begin{array}{c}C_6H_5N\\ |\\ C_6H_5N\end{array}\!\!>O+3H_2O$$

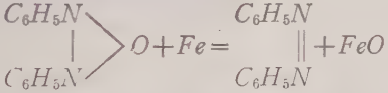
Azoxybenzene forms long, light-yellow needles that melt at 36° C. and are insoluble in water but readily soluble in alcohol and ether. It is reduced on distillation with iron filings to azobenzene, hydrazobenzene, and aniline.

101. Azobenzene, $C_6H_5N{=}N\cdot C_6H_5$.—Azobenzene is obtained when nitrobenzene is reduced by means of zinc dust and caustic soda, or by an alkaline solution of stannous chloride. The reaction, however, must be carried further than in the case of azoxybenzene; thus,



$$2C_6H_5NO_2+8H=\begin{array}{c}C_6H_5N\\ \|\\ C_6H_5N\end{array}+4H_2O$$

It is also obtained by distilling azoxybenzene with iron filings; thus,

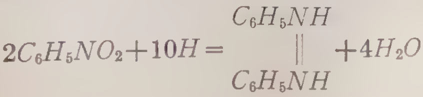


$$\begin{array}{c}C_6H_5N\\ |\\ C_6H_5N\end{array}\!\!>O+Fe=\begin{array}{c}C_6H_5N\\ \|\\ C_6H_5N\end{array}+FeO$$

Azobenzene is recovered as the result of these reactions, in the form of a dark-red oil, which, after a short time, crystallizes in well-defined, orange-red crystals melting at 68° C. and boiling without decomposition at 295° C. It is insoluble in water, soluble in alcohol, and is very stable. Reducing agents convert it into hydrazobenzene and then into aniline, thus showing its constitution.

The azo compounds are, in general, highly colored, and many of them are used as dyes. Those most useful in this way are derivatives of the simple azo compounds.

102. Hydrazobenzene, $C_6H_5NH{-}NHC_6H_5$.—Hydrazobenzene is formed when nitrobenzene is reduced by means of zinc dust and alcoholic potash; thus,



$$2C_6H_5NO_2+10H=\begin{array}{c}C_6H_5NH\\ |\\ C_6H_5NH\end{array}+4H_2O$$

In order to obtain the maximum yield, the reduction is continued to the point where the red color of the azobenzene fades and a colorless liquid is obtained.

Hydrazobenzene forms colorless crystals that have an odor similar to that of camphor. It is soluble in alcohol, slightly soluble in water, and melts at 126° C. Strong reducing agents convert hydrazobenzene into aniline. It oxidizes readily, atmospheric oxygen transforming it into azobenzene. Ferric chloride also oxidizes this substance to azobenzene.

When hydrazobenzene is boiled with mineral acids, a remarkable reaction takes place, as the result of which the benzene nuclei are turned end for end and the compound known as benzidine is formed:

$$C_6H_5NH:NHC_6H_5 \rightarrow NH_2C_6H_4 \cdot C_6H_4NH_2$$

This reaction is known as the *benzidine transformation.*

AMINOAZO COMPOUNDS

103. General Methods of Preparation.—The aminoazo compounds are obtained by the action of a diazonium salt on an aromatic amine and subsequent heating of the diazo amino compound thus formed, with a salt of the amine. They may also be prepared by the reduction of a corresponding nitro compound, such as nitroazobenzene. The aminoazo compounds are of importance because among them are found some of the valuable dyes of commerce.

104. Aminoazobenzene, $C_6H_5N{=}NC_6H_4 \cdot NH_2$.—Aminoazobenzene may be prepared by reducing nitroazobenzene. The latter is formed by nitrating azobenzene; thus,

$$C_6H_5N{=}NC_6H_5 + HNO_3 = C_6H_5N{=}NC_6H_4 \cdot NO_2 + H_2O$$

On subjecting the nitroazo compound to the action of nascent hydrogen, aminoazobenzene is obtained; thus,

$$C_6H_5N{=}NC_6H_4 \cdot NO_2 + 6H = C_6H_5N{=}NC_6H_4 \cdot NH_2 + 2H_2O$$

Aminoazobenzene is best prepared by the action of benzene diazonium chloride on aniline, diazoaminobenzene being formed; thus,

$$C_6H_5N_2 \cdot Cl + C_6H_5NH_2 = C_6H_5N{=}NNH \cdot C_6H_5 + HCl$$

On warming the diazoaminobenzene with aniline hydrochloride, a molecular rearrangement takes place with the formation of aminoazobenzene; thus,

$$C_6H_5N{=}NNH\cdot C_6H_5+C_6H_5NH_2\cdot HCl=C_6H_5N{=}NC_6H_4\cdot NH_2$$
$$+C_6H_5NH_2+HCl$$

105. When prepared by the last method described, aminoazobenzene hydrochloride is obtained in the form of steel-blue needles that are sparingly soluble in water. These crystals dissolve in acid solutions, however, with the formation of a red color, and constitute the dye known as *aniline yellow.* On warming the acid solution of the hydrochloride, the free base, aminoazobenzene, is obtained. It crystallizes from dilute, hot alcoholic solutions that contain a little ammonia, in the form of orange-red crystals that melt at 127° C. Aminoazobenzene is reduced by nascent hydrogen with the formation of aniline and para-phenylenediamine. Thus,

$$C_6H_5N{=}NC_6H_4\cdot NH_2+4H=C_6H_5NH_2+C_6H_4(NH_2)_2$$

Aniline yellow has been used for the purpose of coloring lacquers; but because it lacks the quality of fastness, or, in other words, because of its fugitive character, it is no longer used as dye. It is of importance because of its use in the preparation of dyes that are of commercial value.

106. Acid Yellow or Fast Yellow G.—Acid yellow consists of a mixture of the sodium salts of the monosulphonic and disulphonic acid derivatives of aminoazobenzene. The sulphonic acid derivatives are formed by the action of fuming sulphuric acid on aminoazobenzene; thus,

$$C_6H_5N{=}NC_6H_4\cdot NH_2+2H_2SO_4$$
$$=SO_3H\cdot C_6H_4N{=}NC_6H_3\cdot NH_2\cdot SO_3H+2H_2O$$

The sodium salt, $SO_3Na\cdot C_6H_4N{=}NC_6H_3\cdot NH_2\cdot SO_3Na$, is sparingly soluble in alcohol, but readily soluble in water. It dissolves in hydrochloric acid with the formation of an orange-red solution, and with sulphuric acid it produces a brown-colored solution that turns to a yellow on dilution. In the presence of an acid, a permanent yellow color is imparted to wool and silk by this dye.

107. Fast Yellow R.—Fast Yellow R is the sodium salt of aminoazotoluene disulphonic acid. It has the formula

$$SO_3Na \cdot C_6H_3 \cdot CH_3N{=}NC_6H_2 \cdot NH_2 \cdot CH_3 \cdot SO_3Na$$

This dye imparts a reddish-yellow color to silk or wool in an acid bath. The change of color from the yellow of Acid Yellow to the reddish-yellow of Fast Yellow R is ascribed to the presence of the two methyl groups in the latter.

108. Butter Yellow.—Butter Yellow is the dimethyl derivative of aminoazobenzene. It is obtained by the action of benzene diazonium chloride on dimethylaniline; thus,

$$C_6H_5 \cdot N_2 \cdot Cl + C_6H_5N(CH_3)_2 = C_6H_5N{=}NC_6H_4 \cdot N(CH_3)_2 + HCl$$

Butter Yellow is not soluble in water but is soluble in oils; therefore, it is used for the purpose of coloring oils and butter.

109. Methyl Orange.—Methyl orange, also known as helianthine and tropæolin D, is the sodium salt of para-dimethylaminoazobenzene sulphonic acid. It is prepared by diazotizing para-aminobenzene sulphonic acid (sulphanilic acid) with the formation of the sulphonic acid derivative of benzene diazonium chloride. This compound then combines with dimethylaniline to form para-dimethylaminoazobenzene sulphonic acid. The reactions are represented as follows:

$$SO_3H \cdot C_6H_4 \cdot NH_2 + NaNO_2 + 2HCl =$$

sulphanilic acid

$$SO_3H \cdot C_6H_4 \cdot N_2 \cdot Cl + NaCl + 2H_2O$$

sulphonic acid derivative
of benzene diazonium chloride

$$SO_3H \cdot C_6H_4 \cdot N_2 \cdot Cl + C_6H_5 \cdot N(CH_3)_2 =$$

$$SO_3H \cdot C_6H_4N{=}NC_6H_4 \cdot N(CH_3)_2 + HCl$$

para-dimethylaminoazobenzene
sulphonic acid

The sodium salt of the acid, which is the dye known as methyl orange, is obtained by the operation of salting out, which consists in adding sodium chloride to the solution of the acid. Its formula is $SO_3Na \cdot C_6H_4N{=}NC_6H_4 \cdot N(CH_3)_2$.

Methyl orange is seldom used as a dye because of its fugitive character. It is extensively used as an indicator in analytical chemistry. In neutral or dilute solutions of the alkalies it forms a yellow solution that is immediately changed to a red in the presence of traces of free acid.

110. Diaminoazobenzene, $C_6H_5N{=}NC_6H_3(NH_2)_2$.—Diaminoazobenzene is prepared by the action of benzene diazonium chloride on meta-phenylenediamine. Thus,

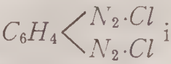
$$C_6H_5N_2 \cdot Cl + C_6H_4(NH_2)_2 = C_6H_5N{=}NC_6H_3(NH_2)_2 + HCl$$

It is a yellow, crystalline base forming a red color when dissolved in acids. Its hydrochloride forms a non-toxic, reddish-brown crystalline powder, soluble in water. It is used under the trade name of *chrysoidine orange* for coloring wool, silk, and cotton an orange color.

111. Triaminoazobenzene, $C_6H_4 \cdot NH_2N{=}NC_6H_3(NH_2)_2$. Triaminoazobenzene is prepared by diazotizing one of the amino groups of meta-phenylenediamine, which results in the formation of the diazonium salt $C_6H_4 \cdot NH_2 \cdot N_2 \cdot Cl$. The diazonium salt then combines with a second molecule of meta-phenylenediamine to form triaminoazobenzene. Thus,

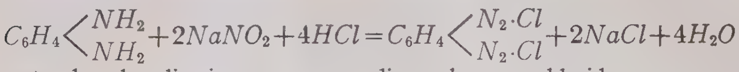
$$C_6H_4 \cdot NH_2 \cdot N_2 \cdot Cl + C_6H_4(NH_2)_2 = C_6H_4 \cdot NH_2N{=}NC_6H_3(NH_2)_2 + HCl$$

112. Bismarck Brown.—Bismarck Brown consists of a mixture of triaminoazobenzene and a new type of compound called, in this case, meta-diaminobenzene dis-azo benzene meta-diaminobenzene.

Meta-phenylenediamine, $C_6H_4(NH_2)_2$, contains two amino groups, and when one of them is diazotized, aminodiazobenzene chloride, $C_6H_4 \cdot NH_2 \cdot N_2 \cdot Cl$, is formed; but when both amino groups are diazotized, a double diazo compound, or a tetrazo compound, having the formula,  $C_6H_4\begin{cases} N_2 \cdot Cl \\ N_2 \cdot Cl \end{cases}$ is formed. This type of compound is also designated by the term *dis-azo*, since the compound contains two azo groups.

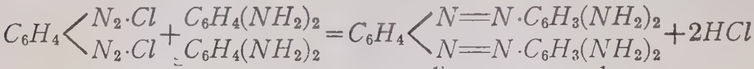
The operation of diazotizing two amino groups is also termed *tetrazotization.*

The reactions according to which the dis-azo compound is produced are represented by the following equations:



$$C_6H_4\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right. + 2NaNO_2 + 4HCl = C_6H_4\left\langle\begin{matrix}N_2\cdot Cl\\N_2\cdot Cl\end{matrix}\right. + 2NaCl + 4H_2O$$

meta-phenylenediamine dis-azo benzene chloride



$$C_6H_4\left\langle\begin{matrix}N_2\cdot Cl\\N_2\cdot Cl\end{matrix}\right. + \begin{matrix}C_6H_4(NH_2)_2\\C_6H_4(NH_2)_2\end{matrix} = C_6H_4\left\langle\begin{matrix}N{=}N\cdot C_6H_3(NH_2)_2\\N{=}N\cdot C_6H_3(NH_2)_2\end{matrix}\right. + 2HCl$$

dis-azo compound

Bismarck Brown is soluble in water and has been used to dye wool, cotton, and leather. The dye is not fast to light or soap, however.

HYDRAZINES

113. Structure.—The hydrazines may be regarded as derivatives of hydrazine, $NH_2—NH_2$, a compound that has never been isolated. As indicated by the foregoing formula, hydrazine contains four replaceable hydrogen atoms, and this fact points to the existence of four classes of compounds, namely: monohydrazines, $R\cdot NH—NH_2$; dihydrazines, $R\cdot NH—NH\cdot R$; trihydrazines, $R_2\cdot N—NH\cdot R$; and the tetrahydrazines, $R_2\cdot N—N\cdot R_2$.

114. Phenylhydrazine, $C_6H_5\cdot NH—NH_2$.—Phenylhydrazine is the simplest derivative of the aromatic hydrazines. It may be prepared by reducing benzene diazonium chloride with stannous chloride in hydrochloric acid solution. The reaction is represented as follows:

$$C_6H_5\cdot N_2\cdot Cl + 4HCl + 2SnCl_2 = C_6H_5NH—NH_2\cdot HCl + 2SnCl_4$$

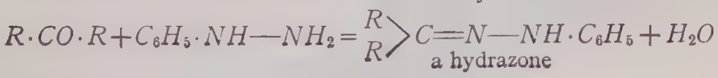
The hydrochloride is obtained as a precipitate, which, after being filtered off is decomposed by strong caustic soda solution when the hydrazine separates as an oily layer. The oil is extracted with ether and the ethereal solution dried with potassium carbonate. The ether is then removed by distillation and the residue of phenylhydrazine is then purified by distillation under diminished pressure.

Phenylhydrazine is a colorless, oily liquid that turns brown on exposure to the air. It has a specific gravity of 1.0978 at

20° C., boils at 243.5° C., and forms crystals that melt at 19.35° C.

Phenylhydrazine is only slightly soluble in water, but dissolves readily in alcohol and in ether. It is a monacid base, and forms salts with the acids; it is a strong reducing agent. Energetic reduction converts it into aniline and ammonia. It reduces alkaline cupric solutions, even in the cold, precipitating yellow cuprous hydroxide and evolving nitrogen, while aniline and benzene are found in the solution. It also reacts with aldehydes and ketones, forming hydrazones. Thus,

$$R\cdot CHO+C_6H_5\cdot NH—NH_2=\underset{\text{a hydrazone}}{R\cdot CH{=}N—NH\cdot C_6H_5}+H_2O$$



$$R\cdot CO\cdot R+C_6H_5\cdot NH—NH_2=\underset{\text{a hydrazone}}{\begin{matrix}R\\R\end{matrix}\!\!>C{=}N—NH\cdot C_6H_5}+H_2O$$

ORGANIC CHEMISTRY
(PART 6)

DERIVATIVES OF THE BENZENE SERIES

HYDROXYL DERIVATIVES

PHENOLS

1. Preparation.—The hydroxy benzenes or phenols are derived from the aromatic hydrocarbons by the replacement of the hydrogen atoms of benzene with hydroxyl groups. The simplest hydroxyl derivative of the series is the compound called phenol, monohydroxy benzene, or carbolic acid. It is represented by the formula C_6H_5OH. Coal tar provides the greatest natural source of the phenols. They can all be made synthetically, however, and when natural sources have not been sufficient to meet the demand, phenol, the most important member of the series, has been made on a large scale by synthetic processes. The reactions involved in these processes are typical and will be used for the purpose of illustration.

Phenols may be prepared by fusing the sodium or potassium salts of the corresponding sulphonic acids with the hydroxides of sodium or potassium; thus,

$$C_6H_5{\cdot}SO_3Na+NaOH=C_6H_5OH+Na_2SO_3$$

By another method, an amino compound, such as aniline, is diazotized and the solution of the diazonium salt formed is warmed, whereupon it decomposes with the formation of a phenol; thus,

$$C_6H_5N_2{\cdot}Cl+H_2O=C_6H_5OH+HCl+N_2$$

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

When a hydrocarbon, such as benzene, is oxidized in the presence of anhydrous aluminum chloride, a phenol is formed; thus,

$$C_6H_6+O=C_6H_5OH$$

2. Properties.—Phenol is represented graphically by the formula shown in Fig. 1, from which it is seen that phenol corresponds to the tertiary alcohols in that it contains the group $C{\cdot}OH$ and not CH_2OH nor $CH{\cdot}OH$. Like the tertiary alcohols, the phenols do not yield aldehydes or ketones on oxidation. The position of the phenols lies midway between the acids and the alcohols. As in the case of alcohols there are monohydroxy phenols, which contain one hydroxyl; dihydroxy phenols, which contain two hydroxyls; and trihydroxy phenols, which contain three hydroxyls.

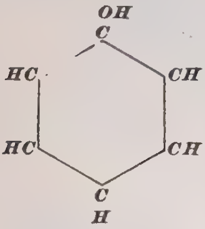


FIG. 1

The phenols have many of the properties of the aliphatic alcohols. They form ethers and ethereal salts. Phosphorus pentachloride causes the exchange of chlorine for their hydroxyl, although this change does not take place as readily as with the aliphatic alcohols. In addition, the phenols have special properties, due to their acid character.

Although the properties of the hydroxyl group are modified to a great extent by union with the phenyl group, the influence of the hydroxyl group on the benzene nucleus is also marked. It increases the readiness with which the remaining hydrogen atoms can be replaced. Dilute nitric acid converts phenol into nitrophenol, while the concentrated acid is required to form nitrobenzene. Bromine at ordinary temperatures reacts with benzene only slowly, but the addition of bromine water to an aqueous solution of phenol immediately precipitates tribromphenol.

The phenols are either liquids or solids, and in many cases have a characteristic odor. Most of the phenols can be distilled without decomposition, and are readily soluble in alcohol and ether. Some also dissolve readily in water. Many of them have antiseptic properties. All have the characteristic property of giving a violet, green, blue or red coloration when ferric chloride is added to their aqueous solutions.

3. Reactions of Phenols.—Because they possess acid properties, the phenols react with the alkalies to form salts called phenolates, or phenates; thus,

$$C_6H_5OH + NaOH = \underset{\substack{\text{sodium}\\ \text{phenolate}}}{C_6H_5 \cdot ONa} + H_2O$$

These salts are alkaline to indicators, such as litmus, and are readily decomposed by carbon dioxide; thus,

$$C_3H_5 \cdot ONa + CO_2 = \underset{\substack{\text{sodium phenyl}\\ \text{carbonate}}}{C_6H_5 \cdot O \cdot COONa}$$

Because of their alcoholic nature, phenols react with phosphorus pentachloride and acetyl chloride in the same manner as do the aliphatic alcohols; thus,

$$C_6H_5OH + PCl_5 = C_6H_5Cl + POCl_3 + HCl$$
$$C_6H_5OH + CH_3COCl = \underset{\text{phenyl acetate}}{C_6H_5COOCH_3} + HCl$$

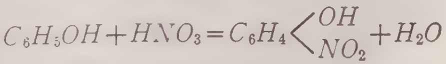
When the phenols are distilled with zinc dust, they are reduced and a hydrocarbon is formed; thus,

$$C_6H_5OH + Zn = C_6H_6 + ZnO$$

On heating a phenol with a compound of zinc chloride and ammonia, $ZnCl_2 \cdot 4NH_3$, an amino compound, is formed; thus,

$$C_6H_5OH + NH_3 = \underset{\text{aniline}}{C_6H_5NH_2} + H_2O$$

When the phenols are treated with a mixture of nitric and sulphuric acids, or what is known as standard mixed acid, they form nitrophenols; thus,



$$C_6H_5OH + HNO_3 = C_6H_4 \begin{matrix} \diagup OH \\ \diagdown NO_2 \end{matrix} + H_2O$$

The reaction in this case is influenced by the presence of the hydroxyl group, and substitution of the nitro group is much more easily effected than when the hydrocarbon itself is nitrated.

MONOHYDROXY PHENOLS

4. Phenol, C_6H_5OH.—Phenol, monohydroxy benzene, or carbolic acid is obtained from coal tar by treating the fraction that distils between 170° C and 230° C. with caustic soda. A crystalline phenolate is formed,

$$C_6H_5OH+NaOH=C_6H_5\cdot ONa+H_2O$$

from which phenol is recovered by treatment with hydrochloric acid; thus,

$$C_6H_5\cdot ONa+HCl=C_6H_5OH+NaCl$$

The product is then purified by distillation.

Phenol can be prepared, also, by melting together potassium benzene sulphonate and caustic potash; thus,

$$C_6H_5\cdot SO_3K+KOH=C_6H_5OH+K_2SO_3$$

Another method for preparing phenol synthetically is to oxidize benzene in the presence of aluminum chloride, when the benzene absorbs oxygen directly; thus,

$$2C_6H_6+O_2=2C_6H_5OH$$

Pure phenol is a colorless crystalline substance that possesses a characteristic odor. It deliquesces on exposure to air and develops a pink color. It is extremely poisonous and has a caustic action on the skin. It is only slightly soluble in water, one part dissolving in about twenty parts of water, but it is soluble in alcohol, ether, and chloroform. It melts at 42° C. and boils at 182° C. The presence of a small percentage of water prevents it from crystallizing. It has valuable antiseptic properties and is extensively used as a disinfectant and in the manufacture of picric acid.

Although phenol has acid properties, these are too weak to decompose alkaline carbonates. It does, however, form definite compounds with the alkalies and with several strong bases. Potassium phenolate, C_6H_5OK, is formed when metallic potassium is dissolved in phenol, or when phenol is treated with a concentrated solution of caustic potash. Barium phenolate, $(C_6H_5O)_2Ba$, is made by dissolving phenol in barium hydroxide. It crystallizes with two molecules of water. An aqueous solution of phenol produces a violet color with ferric chloride.

5. **Cresols,** $C_6H_4\langle{}^{CH_3}_{OH}$.—The cresols, or monohydroxy toluenes, exist in three isomeric forms, namely, ortho-, meta-, and para-cresol. All are found with phenol in coal tar and in the tar obtained from pine and beechwood distillation. They are separated from one another only with difficulty and hence are best prepared from the corresponding toluidines or toluene sulphonic acids. In their properties they resemble phenol very closely.

Ortho-cresol forms white crystals readily soluble in alcohol and ether but sparingly soluble in water. It melts at 30° C. and boils at 191° C.

Para-cresol melts at 36° C., boils at 202° C., is slightly soluble in water, and soluble in alcohol and ether. It forms a crystalline mass with an odor of phenol. It is a product of the decomposition of albumin.

Meta-cresol is a colorless to yellowish liquid, with a phenol-like odor. It is slightly soluble in water, readily soluble in alcohol, and boils at 202° C.

Cresote from coal tar is a mixture of phenol and the cresols. It is a yellowish, oily, clear liquid boiling at about 220° C., and has a specific gravity of 1.07.

6. **Thymol and Carvacrol.**—Thymol and carvacrol, two important isomeric phenols, are monohydroxy derivatives of cymene, $C_6H_4{\cdot}CH_3{\cdot}C_3H_7$. They are represented by the formulas shown in Fig. 2.

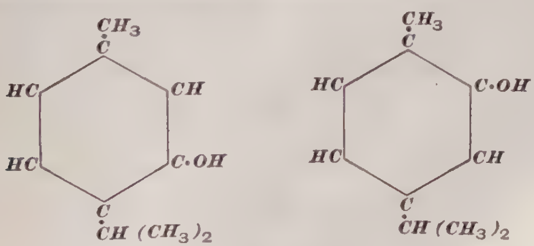


FIG. 2

Thymol is found in oil of thyme. It forms colorless crystals with a thyme-like odor, and a pungent, somewhat caustic taste. It has a specific gravity of .979 at 15° C., melts at 50° C., boils at 232° C., and is soluble in alcohol and ether. It is used as an antiseptic.

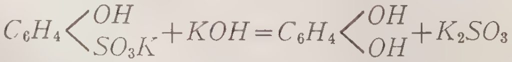
Iodine and caustic potash convert thymol into diiodothymol, which has replaced iodoform to a great extent under the names of aristol and annidalin. Phosphorus pentasulphide converts it into cymene, and treated with phosphorus pentoxide it yields meta-cresol and propylene.

Carvacrol is a colorless liquid found in nature in origanum oil. It can be obtained from oil of caraway by heating the latter with caustic potash or phosphoric acid. Carvacrol melts at 0° C. and boils at 238° C. It has an odor like that of thyme and is used in perfumery.

DIHYDROXY PHENOLS

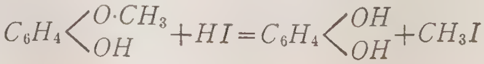
7. Sources and Properties.—The three isomeric, dihydroxy benzenes, namely, catechol, resorcinol, and quinol, are obtained from wood tar. They may be prepared synthetically by fusing the alkali salts of benzene disulphonic acid with the caustic alkalies and by other methods. In most of their ordinary properties they resemble the monohydroxy benzenes. They react more readily, however, than do the simpler phenols.

8. Catechol, $C_6H_4(OH)_2$.—Catechol, or ortho-dihydroxy benzene, also known as pyrocatechol, pyrocatechin, and pyrocatechinol, is a constituent of many resins and derives its name from the fact that it was first obtained by the destructive distillation of a resin called catechu. It may be prepared synthetically by fusing the potassium salt of phenol orthosulphonic acid with caustic potash; thus,



$$C_6H_4\left\langle\begin{array}{l}OH\\SO_3K\end{array}\right.+KOH=C_6H_4\left\langle\begin{array}{l}OH\\OH\end{array}\right.+K_2SO_3$$

It may also be prepared by heating methyl catechol, or guaiacol, $C_6H_4OH{\cdot}O{\cdot}CH_3$, which is obtained from wood tar, with hydriodic acid; thus,



$$C_6H_4\left\langle\begin{array}{l}O{\cdot}CH_3\\OH\end{array}\right.+HI=C_6H_4\left\langle\begin{array}{l}OH\\OH\end{array}\right.+CH_3I$$

Catechol forms colorless crystals that are very soluble in water and alcohol. It melts at 104° C. and boils at 245° C. It possesses acid properties and reacts with the alkalies. A dilute aqueous solution of catechol gives a dark-green color with ferric chloride, that changes to a violet on the addition of a solution of sodium carbonate, and finally to a red. These color reactions are characteristic of all of the dihydroxy phenols. Catechol is a reducing agent, and at ordinary temperatures it precipitates metallic silver from silver nitrate solutions.

9. Resorcinol, $C_6H_4(OH)_2$.—Resorcinol, meta-hydroxy benzene, or resorcin, is obtained from natural sources by fusing certain resins with the alkalies. It is prepared on a large scale by fusing the potassium salt of benzene meta-disulphonic acid with caustic potash. Resorcinol crystallizes from water in prisms or plates readily soluble in water, alcohol, and ether, but insoluble in chloroform and carbon disulphide. It has a sweet taste, melts at 110° C., and boils at 280° C. Its solutions give a dark-purple color with ferric chloride. It absorbs oxygen from the air, becoming brown, and reduces ammoniacal copper and silver solutions. The most characteristic test for resorcinol is to heat it with phthalic anhydride, when it forms a yellowish-red mass. When this is dissolved in dilute sulphuric acid, and ammonium hydroxide is added, a beautiful green fluorescence is produced. Resorcinol is extensively used in the manufacture of certain dyes.

10. Quinol, $C_6H_5(OH)_2$.—Quinol, or para-hydroxy benzene, also known as hydroquinone, is found in nature in the leaves of the bearberry, from which it may be extracted by boiling with water. It is formed by the oxidation of quinic acid, $C_6H_7(OH)_4COOH$, whence it derives its name. The usual method employed for its preparation consists in the reduction of quinone, $C_6H_4O_2$, with sulphurous acid and subsequent extraction of the reaction mixture with ether; thus,

$$C_6H_4O_2+H_2SO_3+H_2O=C_6H_4(OH)_2+H_2SO_4$$

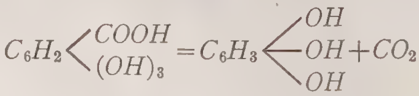
Quinol is a colorless, crystalline substance soluble in alcohol, ether, and hot water, and melts at 169° C. It sublimes in monoclinic tablets, is odorless, and has a sweet taste. Its chief characteristic is the loss on oxidation of two hydrogen atoms with the formation of quinone. It is used as a developer in photography.

11. Orcinol, $C_6H_3\left\langle\begin{matrix}CH_3\\(OH)_2\end{matrix}\right.$.—Orcinol, dihydroxy toluene or 1-methyl 3-5 dihydroxy benzene, is obtained by the fermentation of various lichens. It crystallizes in colorless six-sided prisms, melts at 58° C., and boils at 290° C. It has a sweet taste and is soluble in water, alcohol, and ether. Ferric chloride colors its solution violet. In the presence of ammonia and moist air it absorbs oxygen, yielding orcein, $C_{28}H_{24}N_2O_7$. The alcoholic solution of orcein has a purple color and is used as a mordant in microscopy; the alkaline solutions are a deep violet.

12. Litmus.—Litmus is obtained from the same source as orcinol by treating the lichens with ammonia and potassium carbonate and then allowing the mass to ferment. It is extensively used as an indicator in analytical chemistry. In alkaline solutions it exhibits a blue color that immediately changes to a red in the presence of an acid.

TRIHYDROXY PHENOLS

13. Pyrogallol, $C_6H_3(OH)_3$.—Pyrogallol, 1-2-3 trihydroxy benzene, or pyrogallic acid, is formed when gallic acid is heated; thus,



$$C_6H_2\left\langle\begin{matrix}COOH\\(OH)_3\end{matrix}\right. = C_6H_3\left\langle\begin{matrix}OH\\OH\\OH\end{matrix}\right. + CO_2$$

It is also formed by fusing the potassium salt of parachlorphenol sulphonic acid with caustic potash; thus,

$$C_6H_3Cl{\cdot}OH{\cdot}SO_3K + 2KOH = C_6H_3(OH)_3 + KCl + K_2SO_3$$

Pyrogallol crystallizes in white, lustrous needles soluble in water, alcohol, and ether, melts at 132° C., and boils at 210° C. It is a strong reducing agent, precipitating silver and mercury in a metallic state. Its alkaline solutions rapidly absorb oxygen and turn brown. This property makes it useful for gas analysis. It is also used as a developing agent in photography. Pyrogallol gives no color with ferrous solutions; but if a trace of ferric salt is present, it gives a blue color to the solution.

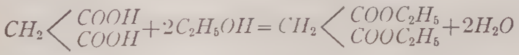
14. Phloroglucinol; $C_6H_3(OH)_3$.—Phloroglucinol, or 1-3-5 trihydroxy benzene, isomeric with pyrogallol, is formed by fusing various resins with caustic potash. It derives its name from the fact that it was first obtained from the glucoside phloridzin and because it possesses a sweet taste. Phloroglucinol is also obtained when either orcinol or benzene 1-3-5 trisulphonic acid is fused with caustic potash.

It forms a white, or slightly yellow, crystalline powder easily soluble in water, alcohol, and ether, and has a very sweet taste. The crystals from an ether solution are anhydrous; those deposited from a water solution contain two molecules of water, which they lose at 100° C. When heated they melt at 218° C. Phloroglucinol sublimes without decomposition. It gives a deep violet coloration with ferric chloride.

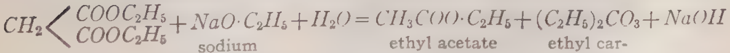
15. Structure of Phloroglucinol.—When sodium ethoxide is heated with diethyl malonate, in the presence of water, ethyl acetate, ethyl carbonate, and sodium hydroxide are the products formed. The ethyl acetate then reacts with a second molecule of diethyl malonate to form diethyl acetone dicarboxylate.

The reactions that take place in the synthesis of phloroglucinol by the foregoing method, may be represented by the following equations:

$$C_2H_5OH + Na = \underset{\text{sodium ethoxide}}{NaO\cdot C_2H_5} + H$$



$$\underset{\text{malonic acid}}{CH_2 \Big\langle {COOH \atop COOH}} + 2C_2H_5OH = \underset{\text{diethyl malonate}}{CH_2 \Big\langle {COOC_2H_5 \atop COOC_2H_5}} + 2H_2O$$

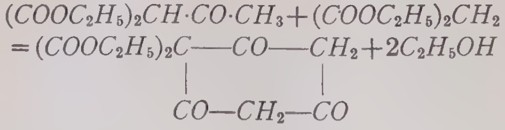


$$CH_2 \Big\langle {COOC_2H_5 \atop COOC_2H_5} + \underset{\text{sodium ethoxide}}{NaO\cdot C_2H_5} + H_2O = \underset{\text{ethyl acetate}}{CH_3COO\cdot C_2H_5} + \underset{\text{ethyl carbonate}}{(C_2H_5)_2CO_3} + NaOH$$

Ethyl acetate reacts with diethyl malonate to form the diethyl ester of acetone dicarboxylic acid; thus,

$$(COOC_2H_5)_2CH_2 + C_2H_5OOC\cdot CH_3$$
$$= \underset{\text{diethyl acetone dicarboxylate}}{(COOC_2H_5)_2CH\cdot CO\cdot CH_3} + C_2H_5OH$$

This product then condenses with another molecule of diethyl malonate, diethyl phloroglucinol dicarboxylate being formed; thus,



$$\begin{array}{l} (COOC_2H_5)_2CH\cdot CO\cdot CH_3+(COOC_2H_5)_2CH_2 \\ =(COOC_2H_5)_2C\text{——}CO\text{——}CH_2+2C_2H_5OH \\ \qquad\qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad\qquad CO\text{—}CH_2\text{—}CO \end{array}$$

diethyl phloroglucinol dicarboxylate

When diethyl phloroglucinol dicarboxylate is fused with caustic potash, hydrogen replaces the ethyl carboxyl groups and phloroglucinol is formed. According to this method for its formation, phloroglucinol should have the structure shown in Fig. 3, and is hexamethylene in which three of the methylene groups, CH_2, have been replaced by carboxyl. It should, therefore, be called triketohexamethylene. In some of its reactions, phloroglucinol behaves as though it had this structure, while again, in some of its reactions, it behaves like a phenol. It can, therefore, also have the structure of a trihydroxy benzene, as shown in Fig. 4. Many cases of this nature are known; and, as previously stated, any substance that reacts as though it had two different structures is said to be *tautomeric*.

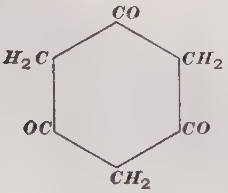


FIG. 3

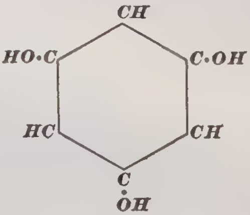


FIG. 4

DERIVATIVES OF PHENOLS

ETHERS

16. Phenyl Methyl Ether, $C_6H_5{\cdot}O{\cdot}CH_3$.—Phenyl methyl ether, or anisol, may be prepared by treating potassium phenolate with methyl iodide; thus,

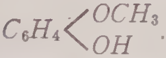
$$C_6H_5OK+CH_3I=C_6H_5{\cdot}O{\cdot}CH_3+KI$$

Phenyl methyl ether is a colorless liquid with a pleasant ethereal odor. Its specific gravity is .992 at 25° C; it is soluble in alcohol and boils at 155° C.

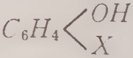
17. Phenyl Ethyl Ether, $C_6H_5{\cdot}O{\cdot}C_2H_5$.—Phenyl ethyl ether, or phenetol, is prepared by a process analogous to that for the preparation of anisol. It is prepared, also, by heating sodium ethyl sulphonate with sodium phenolate:

$$C_2H_5{\cdot}SO_3Na+C_6H_5{\cdot}ONa=C_6H_5{\cdot}O{\cdot}C_2H_5+Na_2SO_3$$

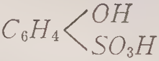
Phenetol is an oily, aromatic liquid, with a specific gravity of .963 at 25° C.; it boils at 172° C., and is soluble in alcohol and ether.

18. Guaiacol,  $C_6H_4\begin{cases}OCH_3\\OH\end{cases}$.—Guaiacol is the monomethyl ether of pyrocatechol. It was first obtained from guaiac resin, from which it derives its name. It is always present in the tar obtained by the destructive distillation of beechwood, and the guaiacol of commerce is obtained from this source. It is sparingly soluble in water, but readily dissolves in alcohol and ether. It crystallizes in hexagonal prisms that melt at 28° C. Liquid guaiacol boils at 205° C. When heated with hydriodic acid, guaiacol breaks down and yields catechol and methyl iodide. It is used in medicine.

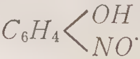
SUBSTITUTED PHENOLS

19. Halogen Phenols,  $C_6H_4\begin{cases}OH\\X\end{cases}$.—The presence of the hydroxyl group in the benzene ring, in the case of a phenol, enables substitution of the halogens to be made much more readily than in the case of benzene itself. Thus, while it is necessary to use a halogen carrier to effect substitution in the benzene molecule, with phenols substitution takes place readily at ordinary temperatures and without the aid of a halogen carrier. When bromine water is brought in contact with phenol, a reaction takes place, and tribromphenol, $C_6H_2OH \cdot (Br)_3$, is formed. Tribromphenol is a crystalline compound that melts at 96° C. It is almost insoluble in water, but dissolves in alcohol and ether. Its formation is used as a test for the presence of phenol.

Substitution of chlorine in a phenol is effected by the use of sulphuryl chloride, SO_2Cl_2, and the iodine substituted phenols are formed by the action of iodine in the presence of hydriodic acid.



20. Phenolsulphonic Acids, $C_6H_4\left\langle\begin{matrix}OH\\SO_3H\end{matrix}\right.$.—The phenol sulphonic acids are formed when phenol is dissolved in concentrated sulphuric acid. If the reaction takes place in the cold, the ortho acid predominates; but on heating or even boiling with water the ortho acid is converted into the para acid. The ortho and para acids are separated by means of their potassium salts. On crystallization, the para-potassium-phenol sulphonate deposits first in hexagonal plates; later the ortho salt separates in prisms. The water solution of ortho-phenol-sulphonic acid is the well-known antiseptic aseptol. Meta-phenol sulphonic acid is obtained when meta-benzene disulphonic acid is heated to 180° C., with an aqueous solution of caustic potash. The free acid crystallizes in fine needles containing two molecules of water.



21. Nitrosophenol, $C_6H_4\left\langle\begin{matrix}OH\\NO\end{matrix}\right.$.—Nitrosophenol may be prepared by the action of nitrous acid on phenol or by the action of a dilute caustic potash solution on para-nitrosodimethylaniline; thus,

$$C_6H_5OH + HNO_2 = C_6H_4OH \cdot NO + H_2O$$

$$(CH_3)_2N \cdot C_6H_4 \cdot NO + H_2O = C_6H_4OH \cdot NO + (CH_3)_2NH$$

These reactions indicate that para-nitrosophenol has the structure represented by the formula shown in Fig. 5. A compound that possesses identical properties is formed, however, by an entirely different reaction. Thus, when quinone, $CO{\cdot}C_4H_4CO$, is boiled with hydroxylamine hydrochloride, a compound is formed that has the structure represented by Fig. 6. This compound is known as quinone monoxime. Para-nitrosophenol and quinone monoxime therefore furnish another example of tautomerism. Para-nitrosophenol crystallizes in fine colorless needles that melt at 125° C. and turn brown on exposure to the air. It dissolves in water, alcohol, and ether, forming a pale-green solution. Oxidizing agents convert it into nitrophenol, and on reduction it forms amino phenol. These reactions indicate that it is nitrosophenol. On the other hand, it reacts with bases as do other oximes.

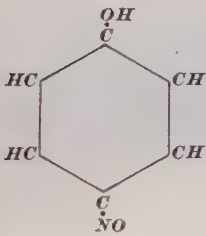


FIG. 5

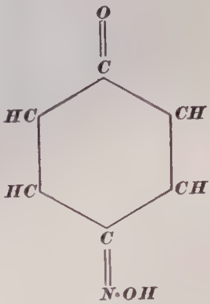
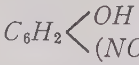


FIG. 6

22. Mononitrophenols, $C_6H_4\begin{matrix} \diagup OH \\ \diagdown NO_2 \end{matrix}$.—The mononitrophenols exist in three isomeric forms. The ortho and para modifications are obtained by the action of dilute nitric acid on phenol. The meta derivative is formed by diazotizing metanitroaniline and then boiling the diazo compound with water.

Ortho-nitrophenol crystallizes in large yellow prisms that melt at 45° C. The liquid boils at 214° C. Ortho-nitrophenol is sparingly soluble in water, but is very soluble in alcohol and ether.

Para-nitrophenol crystallizes from its boiling aqueous solution in long, colorless needles; it melts at 114° C. It is soluble in alcohol and ether, and reddens on exposure to the air. Metanitrophenol is also soluble in water, and can be obtained in yellow crystals melting at 96° C.

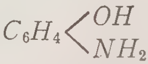
23. Trinitrophenol,  $C_6H_2\langle{}^{OH}_{(NO_2)_3}$.—Trinitrophenol, or picric acid, is the most important of the nitrophenols. It is prepared by dissolving phenol in sulphuric acid and then carefully adding concentrated nitric acid to the solution. By proceeding with the nitration in this manner the formation of tarry substances is avoided. The reactions that take place may be represented as follows:

$$C_6H_5OH+H_2SO_4=C_6H_4OH\cdot HSO_3+H_2O$$
$$C_6H_4OH\cdot HSO_3+3HNO_3=C_6H_2OH(NO_2)_3+H_2SO_4+2H_2O$$

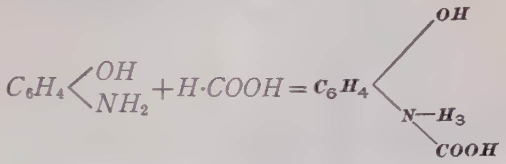
After the violent action has ceased, the mixture is warmed on the water bath as long as red fumes are evolved, and on cooling picric acid crystallizes out.

Pure picric acid crystallizes in yellow, lustrous prisms, without odor but of an intensely bitter taste. It is only slightly soluble in cold water, but more easily soluble in hot water, imparting a bright-yellow color to the solution. It is readily soluble in alcohol and ether, and melts at 122.5° C. It is poisonous, is strongly acid, and decomposes with explosive violence when heated rapidly. Picric acid is the final product of the action of nitric acid on phenol. It is frequently used to dye silk and wool yellow, and as an explosive under the name of lyddite.

Among the salts of picric acid and the metals, which correspond to the general formula $C_6H_2(NO_2)_3\cdot OM$, are potassium picrate and ammonium picrate. Both of these salts explode when heated or struck, and are used as constituents of explosives.

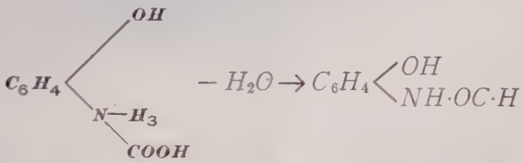
24. Aminophenols,  $C_6H_4\langle{}^{OH}_{NH_2}$.—The aminophenols are the result of the reduction of the nitrophenols by tin and hydrochloric acid. These compounds are so weakened in their acidic character that they do not combine with bases, but form salts with acids. The free amino-phenols are colorless solids crystallizing in leaflets, which turn brown by atmospheric oxidation and yield resin.

Ortho-aminophenol melts at 170° C. and dissolves with difficulty in water. Acid residues can be readily substituted in this compound in the amino group, causing the loss of water and forming anhydro bases; thus,



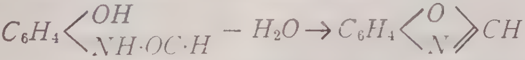
$$C_6H_4\left<\begin{matrix}OH\\NH_2\end{matrix}\right. + H{\cdot}COOH = C_6H_4\left<\begin{matrix}OH\\ \\N{-}H_3\\ \quad COOH\end{matrix}\right.$$

The formic acid salt of ortho-aminophenol formed in this manner readily loses one molecule of water and yields orthoform aminophenol; thus,



$$C_6H_4\left<\begin{matrix}OH\\ \\N{-}H_3\\ \quad COOH\end{matrix}\right. - H_2O \rightarrow C_6H_4\left<\begin{matrix}OH\\NH{\cdot}OC{\cdot}H\end{matrix}\right.$$

When this compound is heated, another molecule of water is lost and the anhydride is formed; thus,



$$C_6H_4\left<\begin{matrix}OH\\NH{\cdot}OC{\cdot}H\end{matrix}\right. - H_2O \rightarrow C_6H_4\left<\begin{matrix}O\\N\end{matrix}\right>CH$$

Para-aminophenol melts at 184° C., with decomposition yielding an ethyl ether, paraphenetidine, $C_6H_4\left<\begin{matrix}OC_2H_5.\\NH_2\end{matrix}\right.$ This ether, treated with glacial acetic acid, forms an acetyl derivative extensively used in medicine under the name phenacetin, $C_6H_4\left<\begin{matrix}OC_2H_5\\NH{\cdot}CO{\cdot}CH_3.\end{matrix}\right.$ An alkaline solution of para-aminophenol is used as a photographic developer (rodinal). Meta-aminophenol is obtained from metanitro-phenol. It melts at 122° C. Many of its derivatives are used in the preparation of the rhodamine dyes.

ALCOHOLS

25. Preparation and Properties.—The aromatic alcohols are derived from the aromatic hydrocarbons, beginning with toluene, by replacing the hydrogen atoms of the side chain with hydroxyl groups. The methods used in their preparation are exactly the same as those employed in the synthesis of the aliphatic alcohols. The reactions that take place in the preparation of benzyl alcohol, $C_6H_5{\cdot}CH_2OH$, the first member of the series, are typical and are represented by the following equations:

When benzyl chloride is heated with water, a dilute solution of an alkali, or with silver hydroxide, benzyl alcohol is formed; thus,

$$C_6H_5{\cdot}CH_2Cl+H_2O=C_6H_5{\cdot}CH_2OH+HCl$$

The same alcohol is formed when benzaldehyde, C_6H_5CHO, is reduced by means of nascent hydrogen, or when it is treated with caustic potash solution; thus,

$$C_6H_5{\cdot}CHO+2H=C_6H_5{\cdot}CH_2OH$$
$$2C_6H_5{\cdot}CHO+KOH=C_6H_5{\cdot}CH_2OH+C_6H_5{\cdot}COOK$$

As far as chemical properties are concerned, the aromatic alcohols are similar in most respects to the aliphatic alcohols. Both exist as primary, secondary, and tertiary alcohols, and under the influence of oxidizing agents give rise to the same classes of products. In their physical properties they differ from the aliphatic alcohols by being much less soluble in water and by possessing higher boiling points.

26. Benzyl Alcohol, $C_6H_5{\cdot}CH_2OH$.—Benzyl alcohol is the typical aromatic alcohol. It is found in nature in storax, and in the balsams of Peru and Tolu. It is prepared in a number of ways:

1. By treating the corresponding aldehyde with nascent hydrogen:

$$C_6H_5{\cdot}CHO+2H=C_6H_5{\cdot}CH_2OH$$

2. By replacing the chlorine of benzyl chloride by hydroxyl, which can be effected by boiling the chloride for some time with water:

$$C_6H_5{\cdot}CH_2Cl+H_2O=C_6H_5{\cdot}CH_2OH+HCl$$

Benzyl alcohol is a colorless liquid with a pleasant aromatic odor; it has a specific gravity of 1.05, is soluble in alcohol and ether, and difficultly soluble in water. It boils at 206° C. Oxidizing agents convert benzyl alcohol first into benzaldehyde and then into benzoic acid. The relation of these substances is the same as that between any primary alcohol and the corresponding aldehyde and acid. Hydriodic acid transforms it into toluene. Phosphorus pentachloride reacts readily with benzyl alcohol, forming benzyl chloride. Although benzyl alcohol forms ethers and esters, it does not form an ester when brought in contact with sulphuric acid, but is converted into a tar-like mass instead, and in this respect it differs from the aliphatic alcohols. Benzyl alcohol does not dissolve in solutions of the alkalies nor does it react with ferric chloride, as do the phenols, with the production of a characteristic color.

ALDEHYDES

PREPARATION AND PROPERTIES

27. Introductory.—The relationship that exists between the aromatic alcohols and aldehydes is the same as that existing between the aliphatic alcohols and aldehydes. Thus, the aromatic aldehydes are derived from the alcohols by the removal of two hydrogen atoms from the CH_2OH group, or, in other words, by the oxidation of a primary alcohol. The reactions by which their formation is accomplished are illustrated by the equations showing the formation of benzaldehyde, $C_6H_5{\cdot}CHO$, the first and most important member of the series.

28. Benzaldehyde, $C_6H_5{\cdot}CHO$.—Benzaldehyde is found in nature associated with glucose and hydrocyanic acid, in a glucoside called amygdalin, which exists in bitter almonds and in the kernels of peach and cherry pits. It may be obtained from these sources by simply mixing the ground kernels with water and allowing the mixture to stand. Under these conditions, amygdalin is hydrolyzed by the action of an enzyme, called emulsin, that is also present in the kernels, and benzaldehyde, glucose, and hydrocyanic acid are set free. Benzaldehyde may be prepared synthetically by several methods, among which are the following:

1. By treating benzal chloride with water and milk of lime:

$$C_6H_5{\cdot}CHCl_2+H_2O=C_6H_5{\cdot}CHO+2HCl$$

2. By oxidizing benzyl alcohol:

$$2C_6H_5{\cdot}CH_2OH+O_2=2C_6H_5{\cdot}CHO+2H_2O$$

3. By distilling a mixture of calcium benzoate and calcium formate:

$$(C_6H_5{\cdot}COO)_2Ca+(H{\cdot}COO)_2Ca=2C_6H_5{\cdot}CHO+2CaCO_3$$

4. By the reduction of benzoyl chloride:

$$C_6H_5{\cdot}COCl+H_2=C_6H_5{\cdot}CHO+HCl$$

5. It is prepared on a large scale by boiling benzyl chloride with an aqueous solution of the nitrates of lead or copper. In this process the benzyl chloride is first converted to benzyl alcohol by the action of the water and the alcohol is then oxidized to aldehyde by the nitrate of the metal; thus,

$$C_6H_5{\cdot}CH_2Cl+H_2O=C_6H_5{\cdot}CH_2OH+HCl$$

$$2C_6H_5{\cdot}CH_2OH+Pb(NO_3)_2+2HCl=2C_6H_5{\cdot}CHO+PbCl_2+N_2O_3+3H_2O$$

29. Benzaldehyde is a colorless liquid that has a specific gravity of 1.05 at 15° C., and boils at 180° C. It is sparingly soluble in water but is miscible with alcohol and ether in all proportions. It may be precipitated from its alcoholic and ethereal solutions by the addition of water. It possesses the odor of oil of bitter almonds and is used for flavoring purposes and in the manufacture of dyes. On contact with air, benzaldehyde reacts with oxygen and is converted into benzoic acid; thus,

$$C_6H_5{\cdot}CHO+O=C_6H_5{\cdot}COOH$$

Reducing agents convert it into benzyl alcohol; thus,

$$C_6H_5{\cdot}CHO+2H=C_6H_5{\cdot}CH_2OH$$

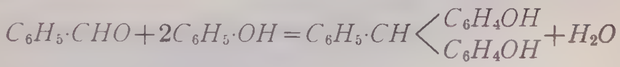
Benzaldehyde is distinguished from the aliphatic aldehydes by its action toward ammonia. When brought in contact with the latter, it does not form a compound analogous to acetaldehydeammonia, but yields a hydroamide; thus,

$$3C_6H_5{\cdot}CHO+2NH_3=\underset{\text{hydrobenzamide}}{(C_6H_5{\cdot}CH)_3N_2}+3H_2O$$

Another characteristic of the aromatic aldehydes is their behavior toward alcoholic potash, one molecule of the aldehyde being oxidized and the other reduced. Thus, in the case of benzaldehyde, the reaction occurs as represented by the equation

$$2C_6H_5{\cdot}CHO+KOH=C_6H_5{\cdot}COOK+C_6H_5{\cdot}CH_2OH$$

With dimethyl aniline or phenols the aromatic aldehydes condense readily, forming derivatives of triphenyl methane; thus,



$$C_6H_5{\cdot}CHO+2C_6H_5{\cdot}OH=C_6H_5{\cdot}CH\left\langle\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}\right.+H_2O$$

HIGHER AROMATIC ALDEHYDES

30. Cinnamic Aldehyde, $C_6H_5{\cdot}CH{:}CH{\cdot}CHO$.—Cinnamic aldehyde occurs as the principal constituent of the volatile oils of cinnamon and cassia. It is prepared synthetically by passing dehydrating agents, such as hydrochloric acid gas, into a mixture of acetaldehyde and benzaldehyde. The reaction that takes place in its formation in this manner is represented as follows:

$$CH_3{\cdot}CHO+C_6H_5{\cdot}CHO=C_6H_5{\cdot}CH{:}CH{\cdot}CHO+H_2O$$

Cinnamic aldehyde is a yellowish, oily liquid with a cinnamon-like odor. It has a specific gravity of 1.1129 at 15° C., boils at 245° C., is sparingly soluble in water, but dissolves in alcohol and ether. It decomposes on distillation, and when exposed to the air, it absorbs oxygen and is converted into cinnamic acid, $C_6H_5CH{:}CH{\cdot}COOH$.

31. Cuminic Aldehyde, $C_6H_5C_3H_7{\cdot}CHO$.—Cuminic aldehyde, cuminol, or 1-4 isopropyl benzaldehyde, is found in the essential oil of caraway. It is a yellow, oily liquid with a strong, persistent, aromatic odor, and an acrid burning taste.

Its specific gravity is .975 at 25° C., it is soluble in alcohol and ether, and boils at 237° C. Its reactions are like those of benzoic aldehyde.

32. Anisic Aldehyde, $C_6H_5{\cdot}OCH_3{\cdot}CHO$.—Anisic aldehyde, or para-methoxybenzaldehyde, is prepared by the oxidation of anise and fennel oils. It is a colorless, fragrant liquid soluble in alcohol and ether; it boils at 248° C. and has a specific gravity of 1.126 at 15° C. It is used in perfumery, mixed with other odorous substances, to obtain an odor resembling that of hawthorn.

33. Salicylic Aldehyde, $C_6H_4OH{\cdot}CHO$.—Salicylic aldehyde or ortho-hydroxy-benzaldehyde is prepared from phenol by treatment with a mixture of chloroform and caustic potash. It is also prepared by oxidizing the glucoside, salicin, with potassium dichromate and sulphuric acid. It is a yellowish to colorless, highly refractive, aromatic oil, and has a specific gravity of 1.165 at 25° C. It is very slightly soluble in water, but soluble in all proportions of alcohol and ether, and boils at 196° C. It stains the skin yellow, and its solution gives an intense violet color with ferric chloride. This, together with its property of easily combining with alkalies to form compounds in which an atom of hydrogen is replaced by the metal:

$$C_6H_4OH{\cdot}CHO + KOH = C_6H_4OK{\cdot}CHO + H_2O$$

indicates this aldehyde to be hydroxybenzaldehyde, and, since the OH group is attached to the benzene nucleus, the compound is a phenol aldehyde.

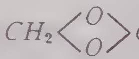
34. Vanillin, $C_6H_3{\cdot}OCH_3{\cdot}OH{\cdot}CHO$.—Vanillin, or meta-methoxy para-hydroxy benzaldehyde, exists naturally in the vanilla bean to the extent of about 2 per cent. It is extracted from the bean by means of boiling alcohol. Vanillin was first prepared synthetically by the oxidation of coniferyl alcohol, $C_6H_3OH{\cdot}OCH_3{\cdot}CH{:}CHCH_2OH$, which is obtained by hydrolysis of the glucoside coniferin contained in the sap of certain cone-bearing trees such as the pine. It may also be prepared by the oxidation of eugenol, $C_6H_3OH{\cdot}OCH_3{\cdot}CH_2{\cdot}CH{:}CH_2$, the chief constituent of oil of cloves.

Vanillin is also formed by what is known as the Reimer-Tiemann reaction, which consists in treating a salt of a phenol with chloroform in the presence of an alkali such as caustic soda. Thus, when the sodium salt of guaiacol, $C_6H_4OH\cdot OCH_3$, is treated in this manner, vanillin is obtained; thus,

$$C_6H_4ONa\cdot OCH_3+CHCl_3+3NaOH=C_6H_3\cdot OCH_3\cdot ONa\cdot CHO \\ +3NaCl+2H_2O$$

$$C_6H_3\cdot OCH_3\cdot ONa\cdot CHO+HCl=C_6H_3\cdot OCH_3\cdot OH\cdot CHO+NaCl$$

Vanillin crystallizes in colorless prisms having a pleasant aromatic odor and an agreeable taste. It melts at 80° C., boils at 285° C., and sublimes readily. It is sparingly soluble in water but readily soluble in alcohol and ether. Vanillin is used in perfumes and as a flavoring material.

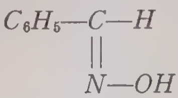
35. Piperonal,  $CH_2\left\langle {}^{O}_{O} \right\rangle C_6H_3\cdot CHO$.—Piperonal, or heliotropin, is obtained by the oxidation of piperic acid, a product of the decomposition of piperine, a constituent of pepper. Piperonal is the methylene ether of protocatechuic aldehyde, $C_6H_3(OH)_2CHO$. Piperonal forms white, shining crystals soluble in alcohol and ether, and only slightly soluble in water. It melts at 37° C. and boils at 263° C. It is used in perfumery under the name of heliotropin.

BENZALDOXIMES

36. Hydroxylamine reacts with benzaldehyde, as with other aldehydes, to form an oxime; thus,

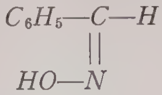
$$C_6H_5\cdot CHO+H_2NOH=C_6H_5\cdot CH{=}N\cdot OH+H_2O$$

Benzaldoxime, $C_5H_5\cdot CH{=}N\cdot OH$, is at first an oil, but when it is purified it forms long, lustrous prisms, which melt at 35° C. When an ethereal solution of this oxime is treated with hydrochloric-acid gas, and the product thus obtained is treated with sodium carbonate, an isomeric oxime is obtained. This crystallizes from ether in thin, lustrous needles and melts at 128° C. When the oxime that melts at 35° C. is treated with acetic anhydride, it yields an acetyl derivative, while under the same conditions, the oxime that melts at 128° C. loses water and forms benzonitrile. The two oximes are regarded as stereoisomeric and are represented by the formulas



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ N-OH \end{array}$$

(1)



$$\begin{array}{c} C_6H_5-C-H \\ \| \\ HO-N \end{array}$$

(2)

The names assigned to the two oximes are benz-*syn*-aldoxime and benz-*anti*-aldoxime. The word *syn* refers to the fact that the hydrogen of the aldehyde group and the hydroxyl group are on the same side of the formula, while the word *anti* indicates that these groups are on opposite sides of the formula. The formula assigned to each oxime is determined by the fact that the one melting at 128° C. readily loses water and the one that melts at 35° C. does not. Thus, formula (1) is given to the former and formula (2) to the latter, since it is assumed that water would be more easily lost by benz-syn-aldoxime with the hydrogen and hydroxyl groups occupying positions on the same side of the formula, than by benz-anti-aldoxime, in the formula for which the hydrogen atom and the hydroxyl groups are on opposite sides.

KETONES

37. General Preparation.—The ketones of the benzene series are analogous in every respect to those of the paraffin series, and they are made in the same way. Acetone is made by the distillation of calcium acetate, and in the same way benzophenone, or diphenyl ketone, is made by distilling calcium benzoate.

Again, mixed ketones of the aliphatic series are obtained by distilling a mixture of the salts of two fatty acids, and in the same way mixed ketones containing a benzene hydrocarbon residue and a paraffin hydrocarbon residue, or two different benzene hydrocarbon residues, may be obtained.

38. Acetophenone, $C_6H_5 \cdot CO \cdot CH_3$.—Acetophenone, or phenymethyl ketone, may be prepared by distilling a mixture of calcium acetate and calcium benzoate; thus,

$$(CH_3COO)_2Ca + (C_6H_5COO)_2Ca = 2C_6H_5 \cdot CO \cdot CH_3 + 2CaCO_3$$

It may also be prepared by treating a mixture of benzene and aluminum chloride with acetyl chloride; thus,

$$C_6H_6+CH_3{\cdot}COCl=C_6H_5{\cdot}COC{\cdot}H_3+HCl$$

The operation is carried out by placing the benzene and aluminum chloride in a flask immersed in ice water and equipped with a reflux condenser and a dropping funnel through which the acetyl chloride is introduced, drop by drop, into the flask. When all of the acetyl chloride has been added, the reaction mixture is allowed to stand for an hour to complete the reaction. The contents of the flask are then poured on ice contained in another vessel. Benzene is then added to this vessel and the acetophenone extracted. After the benzene solution is washed with a dilute solution of caustic soda and then with water, it is dried by being allowed to stand over anhydrous calcium chloride and is then distilled. Acetophenone boils at 202° C. and melts at 20.5° C. It is used in medicine as a soporific, hypnotic, or sleep producer, for which reason the name hypnone is sometimes given to it.

39. Benzophenone, $C_6H_5{\cdot}CO{\cdot}C_6H_5$.—Benzophenone, or diphenyl ketone, is obtained when calcium benzoate is distilled; thus,

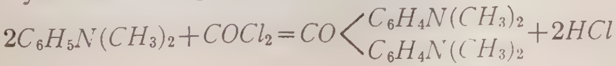
$$(C_6H_5COO)_2Ca=C_6H_5{\cdot}CO{\cdot}C_6H_5+CaCO_3$$

It may also be prepared by treating benzene with benzoyl chloride or with carbonyl chloride in the presence of aluminum chloride; thus,

$$C_6H_6+C_6H_5{\cdot}COCl=C_6H_5{\cdot}CO{\cdot}C_6H_5+HCl$$
$$2C_6H_6+COCl_2=C_6H_5{\cdot}CO{\cdot}C_6H_5+2HCl$$

Benzophenone exists in two allotropic modifications and is therefore dimorphous. One form melts at 48° C. and the other at 26° C. Both forms boil at 306° C. Each is soluble in alcohol and ether.

40. Tetramethyldiaminobenzophenone, $(CH_3)_2N{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}N(CH_3)_2$.—Tetramethyldiaminobenzophenone, or, as it is better known, Michler's ketone, is obtained by treating dimethylaniline with phosgene; thus,



$$2C_6H_5N(CH_3)_2+COCl_2=CO\Big\langle\begin{array}{l}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}+2HCl$$

It is very soluble in alcohol and ether and crystallizes in glittering leaflets. It melts at 174° C., and boils above 360° C., with decomposition. Michler's ketone is used in the preparation of a number of important dyes.

QUINONES

41. Derivation and Structure.—The quinones are compounds derived from benzene by the substitution of two atoms of oxygen for two atoms of hydrogen. This replacement takes place in either the ortho or the para position. Replacement in the meta position is not known. The true quinones are the para-quinones. They may be considered either as derivatives of benzene or as derivatives of dihydrobenzene, the formula for which is shown in Fig. 7.

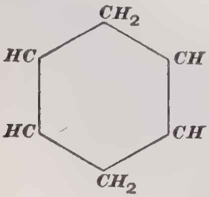


FIG. 7

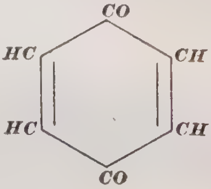


FIG. 8

The simplest example of this class is benzoquinone, or quinone, the constitution of which is expressed by the formula of Fig. 8. This formula requires that quinone should be a diketone and contain two double bonds. These conditions are fulfilled by its properties, its diketonic character being proved by its forming a dioxime. Its ability to take up four atoms of bromine or chlorine, and two molecules of hydrochloric or hydrobromic acid proves the double linking.

42. Benzoquinone, $C_6H_4O_2$.—Benzoquinone was first obtained by the oxidation of quinic acid with manganese peroxide and sulphuric acid. It is obtained also by the oxidation of para-dihydroxybenzene (hydroquinone), para-aminophenol, sulphanilic acid, and para-phenol-sulphonic acid. The ordinary method of preparation is to oxidize aniline with chromic acid.

Benzoquinone crystallizes in long, brilliant needles of golden-yellow color, and has a peculiar, pungent odor. It melts at 116° C. to a yellow liquid that attacks the skin and stains it brown. It volatilizes with steam with partial decomposition, is soluble in alcohol and ether, and only slightly soluble in water. Quinone acts as an oxidizing agent.

43. Tetrachlorquinone, $C_6Cl_4O_2$.—Tetrachlorquinone, or chlorinal, is obtained, together with trichlorquinone, by the action of chlorine on many benzene derivatives, such as phenol, isatine, aniline, etc. The tetrachlorquinone and the trichlorquinone are separated by converting them into the corresponding chlorhydroquinones by the action of sulphurous acid. The tetrachlorhydroquinone, $C_6Cl_4(OH)_2$, is insoluble in water, whereas the trichlor derivative dissolves. The insoluble compound is then oxidized, with strong nitric acid, into chloranil.

Chloranil crystallizes in golden-yellow, shining leaflets soluble in benzene and ether, insoluble in water, and only sparingly soluble in alcohol. Concentrated acids have no effect on it It is used as an oxidizing agent, and in the manufacture of coal-tar dyes. It dissolves in caustic potash, forming a purple-red color, and yielding purple crystals of potassium chloranilate, $C_6Cl_2(OK)_2O_2$. This salt is sparingly soluble in water, but dilute hydrochloric acid dissolves it with the separation of chloranilic acid, $C_6Cl_2(OH)_2O_2$, in the form of shining, reddish needles.

ACIDS

MONOBASIC ACIDS AND DERIVATIVES

44. Introductory.—The aromatic acids result from the replacement of hydrogen in benzene or its homologues by the carboxyl group. This group is either linked directly to the nucleus or is linked to the side chain. Thus, with the homologues of benzene, two classes of compounds are possible. These may be illustrated by toluic acid, $C_6H_4{\cdot}CH_3{\cdot}COOH$, and phenylacetic acid, $C_6H_5{\cdot}CH_2COOH$. Most of the acids of the series are found in nature as constituents of plant and animal products. They may be prepared by the methods of preparation given for benzoic acid.

45. Benzoic Acid, $C_6H_5{\cdot}COOH$.—Benzoic acid, as indicated by its formula, is a monobasic acid. It is the simplest member of the series in which the carboxyl group, $COOH$, is directly linked to the benzene nucleus. Benzoic acid occurs free in gum benzoin, in the balsams of Peru and Tolu, and in combination with glycocoll in the urine of herbivorous animals. It can be prepared in many ways, the most important of which are:

1. By the oxidation of any aromatic hydrocarbon containing a side chain; thus,

$$2C_6H_5{\cdot}CH_3+3O_2=2C_6H_5{\cdot}COOH+2H_2O$$

2. By the oxidation of aromatic alcohols and aldehydes such as benzyl alcohol or benzaldehyde; also, by the oxidation of alcohols, aldehydes, or ketones with side chains, or from all compounds containing a side chain with one carbon atom directly linked to the benzene nucleus; thus,

$$\begin{aligned}&C_6H_5{\cdot}CH_2OH &&\rightarrow C_6H_5{\cdot}COOH\\ &C_6H_5{\cdot}CH_2{\cdot}CH_2OH &&\rightarrow C_6H_5{\cdot}COOH\\ &C_6H_5{\cdot}CHO &&\rightarrow C_6H_5{\cdot}COOH\end{aligned}$$

3. By treating benzene with carbonyl chloride in the presence of aluminum chloride; thus,

$$C_6H_6+COCl_2=C_6H_5{\cdot}COCl+HCl$$
$$C_6H_5{\cdot}COCl+H_2O=C_6H_5{\cdot}COOH+HCl$$

4. By treating benzonitrile with sulphuric acid; thus,

$$C_6H_5CN+2H_2O=C_6H_5{\cdot}COOH+NH_3$$

5. By the action of carbon dioxide on benzene in the presence of aluminum chloride:

$$C_6H_6+CO_2=C_6H_5{\cdot}COOH$$

Benzoic acid was formerly prepared by the sublimation of gum benzoin, and this is still the method by which some benzoic acid is prepared. In the manufacture of benzoic acid on a large scale, however, toluene is converted into benzyl chloride, and this is oxidized with dilute nitric acid.

46. Properties.—Benzoic acid is a white solid crystallizing in lustrous needles or in feathery scales. It is inodorous when cold, but has a faint odor when warmed. It melts at 121° C., sublimes readily at a temperature a little above its melting point, and boils at 250° C. It is only slightly soluble in cold water, but dissolves readily in hot water and in alcohol. It is volatile with steam and can be purified by distillation with steam. Its vapor has a peculiar odor and causes coughing.

Benzoic acid forms many salts, nearly all of which are soluble in water. Heated with lime, benzoic acid is decomposed into benzene and carbon dioxide, the latter uniting with the lime; thus,

$$C_6H_5{\cdot}COOH+CaO=C_6H_6+CaCO_3$$

Sodium amalgam reduces benzoic acid to benzyl alcohol, whereas hydriodic acid and phosphorus reduce it to toluene.

Benzoic acid readily yields substitution products with the halogens, with sulphuric acid, and with nitric acid. When the substitution is direct, the products are mostly meta compounds.

Substitution products of benzoic acid may also be obtained by the oxidation of the corresponding substituted toluenes.

47. Benzoyl Chloride, $C_6H_5{\cdot}COCl$.—Benzoyl chloride is obtained by the action of phosphorus pentachloride on benzoic acid; thus,

$$C_6H_5{\cdot}COOH+PCl_5=C_6H_5{\cdot}COCl+POCl_3+HCl$$

It is a liquid of a disagreeable odor, but is more stable than the corresponding compound of the fatty acids, although it undergoes, in general, the same kind of change. It acts on hydroxyl compounds in the same way that acetyl chloride does, introducing the benzoyl group into compounds; thus,

$$C_6H_5{\cdot}COCl+C_6H_5{\cdot}OH=C_6H_5{\cdot}CO{\cdot}O{\cdot}C_6H_5+HCl$$

The operation is termed *benzoylation.*

48. Benzoic Anhydride, $C_6H_5CO{\cdot}O{\cdot}COC_6H_5$.—Benzoic anhydride is formed by the action of benzoyl chloride on a benzoate; thus,

$$C_6H_5{\cdot}COONa+C_6H_5{\cdot}COCl=C_6H_5CO{\cdot}O{\cdot}COC_6H_5+NaCl$$

This substance is very stable toward water at ordinary temperatures, but when boiled with water is decomposed, yielding benzoic acid.

49. Toluic Acids, $C_6H_4 \cdot CH_3 \cdot COOH$.—The toluic or monomethyl benzoic acids derived from toluene by the substitution of the carboxyl group in the benzene nucleus are three in number. They may be prepared by the partial oxidation of the corresponding xylenes; thus,

$$2C_6H_4 \begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix} + 3O_2 = 2C_6H_4 \cdot CH_3 \cdot COOH + 2H_2O$$

Ortho-toluic acid forms white needles that melt at 102° C. and are soluble in water and alcohol.

Meta-toluic acid crystallizes in white, needle-shaped crystals. It is more soluble in water than either the ortho or the para acid, and is also soluble in alcohol and ether. It melts at 109° C.

Para-toluic acid crystallizes in transparent needles which melt at 180° C. It is soluble in alcohol and ether, boils at 275° C., and is volatile in steam. It is one of the oxidation products of the turpentine oils.

50. Mesitylenic Acid, $C_6H_3 \cdot (CH_3)_2 \cdot COOH$.—Mesitylenic acid, or dimethyl benzoic acid, is formed when mesitylene is oxidized with dilute nitric acid. It is a crystalline, volatile acid, fusing at 166° C., and soluble in boiling water and in alcohol. By distillation with lime it yields meta-xylene. Further oxidation of mesitylenic acid yields uvitic acid, $C_6H_3CH_3(COOH)_2$, and trimesitic acid, $C_6H_3(COOH)_3$.

51. Phenyl Acetic Acid, $C_6H_5 \cdot CH_2 \cdot COOH$.—Phenyl acetic, or, as it is sometimes called, alpha-toluic acid, is the simplest aromatic acid in which the carboxyl group is substituted in the side chain. It is prepared by boiling benzyl cyanide with caustic potash solution. It can be easily distinguished from the toluic acids by oxidation, which converts it into benzoic acid, whereas the toluic acids yield the diabasic phthalic acids.

Phenyl acetic acid crystallizes in shining, thin, white plates soluble in alcohol, ether, and hot water. It melts at 76° C. and boils at 262° C.

52. Hydrocinnamic Acid, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.—Hydrocinnamic acid, the second member of the series in which the carboxyl group is substituted in the side chain, is obtained by the reduction of cinnamic acid with sodium amalgam; thus,

$$C_6H_5CH{:}COOH+2H=C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$$

It crystallizes from water in long, white needles, is readily soluble in alcohol and ether, slightly soluble in water, melts at 47° C., and boils at 280° C. Oxidizing agents convert it into benzoic acid.

UNSATURATED MONOBASIC ACIDS

53. Cinnamic Acid, $C_6H_5CH{:}CH{\cdot}COOH$.—Cinnamic acid, or phenyl acrylic acid, occurs naturally in the balsams of Peru and Tolu and in storax. It is one of the most important of the unsaturated aromatic acids and may be prepared by what is known as Perkin's reaction, which consists in heating a mixture of an aldehyde, the sodium salt of a fatty acid, and the anhydride of the acid. Perkin's reaction is commonly used in the preparation of unsaturated aromatic acids. Thus, cinnamic acid is synthesized by heating together benzaldehyde, sodium acetate, and acetic anhydride at 180° C., for about 15 hours. The anhydride acts as a condensing agent and causes condensation to take place between the benzaldehyde and sodium acetate. The reactions may be represented as follows:

$$C_6H_5CHO+CH_3COONa=C_6H_5CH{:}CH{\cdot}COONa+H_2O$$

$$(CH_3CO)_2O+H_2O=2CH_3COOH$$

$$C_6H_5CH{:}CH{\cdot}COONa+CH_3COOH=C_6H_5CH{:}CH{\cdot}COOH \\ +CH_3COONa$$

Cinnamic acid is soluble in alcohol, ether, and boiling water. On cooling of the water solution, the acid crystallizes in needles that melt at 133° C. In its chemical behavior, cinnamic acid resembles acrylic and other unsaturated acids. Thus, when dissolved in a sodium carbonate solution, it decolorizes a dilute solution of potassium permanganate. Nascent hydrogen converts cinnamic acid into hydrocinnamic acid. Cinnamic acid is used in the preparation of perfumes.

54. Phenyl Propiolic Acid, $C_6H_5C{:}C{\cdot}COOH$.—Phenyl propiolic acid, which contains a triple bond, may be prepared by the oxidation of the acetylene hydrocarbon, phenyl propine, $C_6H_5C{:}C{\cdot}CH_3$. It is also obtained by the reaction between phenyl dibrompropionic acid, $C_6H_5CHBr{\cdot}CHBr{\cdot}COOH$, and alcoholic potash; thus,

$$C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}COOH+2KOH=C_6H_5C{:}C{\cdot}COOH \\ +2KBr+2H_2O$$

Phenyl propiolic acid is a solid that melts at 136° C. It is sparingly soluble in water but dissolves readily in alcohol and ether. It is of importance because of the use of its nitro derivative in the synthesis of indigo.

55. Ortho-Nitrophenyl Propiolic Acid, $C_6H_4NO_2C{:}C{\cdot}COOH$.—Ortho-nitrophenyl propiolic acid is obtained from cinnamic acid by a series of reactions. Cinnamic acid is first nitrated, ortho and para-nitrocinnamic acids being formed; thus,

$$C_6H_5CH{:}CH{\cdot}COOH+HNO_3=C_6H_4NO_2CH{:}CH{\cdot}COOH+H_2O$$

Separation of these acids is effected by converting them into their ethyl esters and then taking advantage of the differences in solubility of the esters. The ester of the ortho acid is then hydrolyzed and the free acid that results is treated with bromine, ortho-nitrophenyl dibrompropionic acid being formed; thus,

$$C_6H_4NO_2CH{:}CH{\cdot}COOH+Br_2=C_6H_4NO_2CHBr{\cdot}CHBr{\cdot}COOH$$

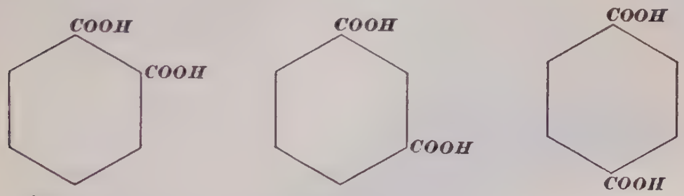
When this acid is treated with caustic potash solution, ortho-nitrophenyl propiolic acid is obtained; thus,

$$C_6H_4NO_2CHBr{\cdot}CHBr{\cdot}COOH+2KOH=C_6H_4NO_2C{:}C{\cdot}COOH \\ +2KBr+2H_2O$$

When ortho-nitrophenyl propiolic acid is heated with an alkali and glucose, indigo is formed.

DIBASIC ACIDS AND DERIVATIVES

56. Phthalic Acids, $C_6H_4(COOH)_2$.—The isomeric dibasic phthalic acids are three in number. They are obtained by the oxidation of the methyl groups of the corresponding xylenes but owe their name to the fact that one of them can be obtained from naphthalene, $C_{10}H_8$. They are colorless, crystalline compounds, and, in general, possess the usual properties of acids. Thus, they form neutral and acid salts and esters, acid amides, and amino acids. The structural formulas of the phthalic acids are represented as shown in Fig. 9.



phthalic acid or ortho-phthalic acid

isophthalic acid or meta-phthalic acid

terephthalic acid or para-phthalic acid

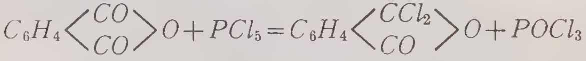
Fig. 9

57. Ortho-Phthalic Acid.—Ortho-phthalic acid, or simply phthalic acid, is formed by the oxidation of naphthalene or naphthalene tetrachloride. On a large scale it is made by the action of fuming sulphuric acid on naphthalene in the presence of a catalyst such as a salt of cerium or thorium. Phthalic acid crystallizes in rhombic prisms only slightly soluble in cold water but readily soluble in hot water, alcohol, and ether. When heated it melts at 184° C., with loss of one molecule of water and the formation of phthalic anhydride, which melts at 128° C.

The formation of an anhydride distinguishes ortho-phthalic acid from the meta and para varieties. On distillation with an excess of lime, it yields benzene, but when exactly two molecules of the acid are heated with one molecule of lime, benzoic acid is formed. Chromic acid decomposes phthalic acid into water and carbon dioxide.

58. Phthalic Anhydride and Phthalimide.—As has been stated, phthalic anhydride, $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$, is obtained by heating phthalic acid. It forms long, shining needles soluble in hot water, alcohol, and ether. It melts at 128° C., and boils at 284° C. Phthalic anhydride unites directly with the phenols, with the aid of heat, with the elimination of water and the formation of the important phthalein dyes. When phthalic anhydride is dissolved in ammonium hydroxide, the solution evaporated to dryness, and the residue fused, a compound known as phthalimide, $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$, is formed. Phthalimide melts at 233.5° C., and may be sublimed. It is used in one method for the preparation of synthetic indigo.

59. Phthalyl Chloride, $C_6H_4(COCl)_2$.—Phthalyl chloride is formed when a mixture consisting of one molecule of phthalic anhydride and one molecule of phosphorus pentachloride is heated; thus,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O+PCl_5=C_6H_4\left\langle\begin{matrix}CCl_2\\CO\end{matrix}\right\rangle O+POCl_3$$

It is a colorless oily liquid having a specific gravity of 1.42 at 15° C. and boils at 281.5° C. It is soluble in ether but reacts with water to form phthalic acid. On reduction with sodium amalgam, chlorine is replaced by hydrogen with the formation of a compound known as phthalide, $C_6H_4\left\langle\begin{matrix}CH_2\\CO\end{matrix}\right\rangle O$.

60. Isophthalic and Terephthalic Acids.—Isophthalic and terephthalic acids are of little importance. Isophthalic acid is obtained when meta-xylene is oxidized with nitric acid or by the oxidation of meta-toluic acid with alkaline potassium permanganate solution. It is soluble in hot water and crystallizes in fine needles. It melts above 300° C., and sublimes unchanged. It does not form an anhydride.

Terephthalic acid may be prepared by the oxidation of paraxylene or para-toluic acid. It is usually obtained as a white powder, and is almost insoluble in water, alcohol, and ether.

It does not melt at normal pressure, but sublimes at high temperatures without decomposition. Like isophthalic acid, it does not yield an anhydride.

NITRO AND AMINO ACIDS AND DERIVATIVES

61. Nitrobenzoic Acids, $C_6H_4NO_2COOH$.—The nitrobenzoic acids, three in number, are obtained when benzoic acid is nitrated; thus,

$$C_6H_5COOH + HNO_3 = C_6H_4NO_2 \cdot COOH + H_2O$$

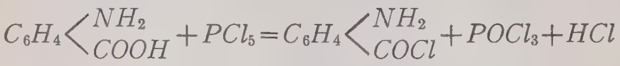
Ortho-nitrobenzoic acid is also obtained by the oxidation of ortho-nitrotoluene, $C_6H_4NO_2CH_3$, with an alkaline potassium permanganate solution. It forms yellowish-white needles soluble in alcohol and ether, that melt at 147° C., and have an intensely sweet taste.

Meta-nitrobenzoic acid is the chief product of the action of nitric acid on benzoic acid. It crystallizes in yellowish-white needles or flakes that melt at 141° C. and are soluble in alcohol and ether.

Para-nitrobenzoic acid is best prepared by the oxidation of the corresponding nitrotoluene. It forms yellowish-white needles soluble in alcohol and ether and melting at 238° C. Of the three nitrobenzoic acids, this is much less soluble in water than the others.

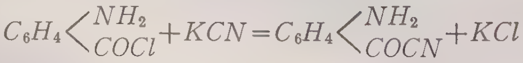
62. Anthranilic Acid, $C_6H_4NH_2 \cdot COOH$.—Anthranilic acid, or ortho-aminobenzoic acid, is the most important of the aminobenzoic acids. It is prepared either by the oxidation of indigo or by the reduction of ortho-nitrobenzoic acid with tin and hydrochloric acid. This acid breaks up easily into aniline and carbon dioxide. It has all of the characteristics of an amino acid, forming salts with both acids and bases. Anthranilic acid forms yellowish crystals soluble in water and alcohol and melting at 144° C. It can be sublimed without decomposition. It has a sweet taste and slightly antiseptic properties. The methyl ester of anthranilic acid, methyl anthranilate, $C_6H_4NH_2COOCH_3$, has a powerful but agreeable odor and is responsible for the fragrance of certain flowers. It is a constituent of oil of orange blossoms and oil of jasmine flowers and is used in the manufacture of perfumes.

63. Isatin, $C_6H_4{<}\substack{NH\\CO}{>}CO$.—Isatin is obtained when indigo is oxidized. It is prepared from ortho-aminobenzoic acid by a series of reactions. Thus, ortho-amino benzoyl chloride is first formed,



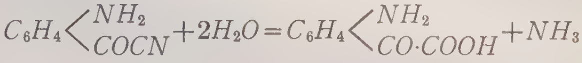
$$C_6H_4{<}\substack{NH_2\\COOH}+PCl_5=C_6H_4{<}\substack{NH_2\\COCl}+POCl_3+HCl$$

This compound is then converted into the nitrile by means of potassium cyanide,



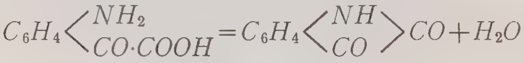
$$C_6H_4{<}\substack{NH_2\\COCl}+KCN=C_6H_4{<}\substack{NH_2\\COCN}+KCl$$

On hydrolysis of the nitrile, ortho-amino benzoyl formic acid is formed,



$$C_6H_4{<}\substack{NH_2\\COCN}+2H_2O=C_6H_4{<}\substack{NH_2\\CO\cdot COOH}+NH_3$$

This acid then loses water, yielding isatin,



$$C_6H_4{<}\substack{NH_2\\CO\cdot COOH}=C_6H_4{<}\substack{NH\\CO}{>}CO+H_2O$$

The formula that has been given for isatin represents it as the anhydride of ortho-aminobenzoyl formic acid. This structure is characteristic of the ortho compounds, as neither the meta nor the para acid forms anhydrides. This is regarded as an argument in favor of the view that in the ortho compounds the two substituting groups are actually nearer together than in the other two compounds. Isatin, however, reacts with some reagents as though it contained the hydroxyl group. It is therefore tautomeric and may also be represented by the formula, $C_6H_4{<}\substack{CO\\N}{\gg}C\cdot OH$. Isatine forms yellowish-red crystals with a bitter taste; it melts at 200° C., and is soluble in alcohol but only slightly soluble in water.

64. Hippuric Acid, $C_6H_5CO\cdot NH\cdot CH_2COOH$.—Hippuric acid, also known as benzoyl amino acetic acid, or benzoyl glycocoll, occurs in the urine of cows, horses, camels, and sheep and in small quantities in human urine. It is prepared synthetically by heating benzamide with chloracetic acid:

$$CH_2Cl{\cdot}COOH + C_6H_5CO{\cdot}NH_2 = C_6H_5CO{\cdot}NH{\cdot}CH_2COOH + HCl$$

by heating glycine and benzoic acid to 160° C.:

$$C_6H_5COOH + CH_2NH_2{\cdot}COOH = C_6H_5CO{\cdot}NH{\cdot}CH_2COOH + H_2O$$

and by heating benzoyl chloride with silver glycocoll:

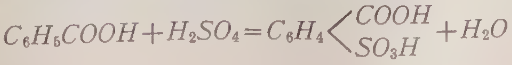
$$CH_2{\cdot}NH_2{\cdot}COOAg + C_6H_5COCl = C_6H_5CO{\cdot}NH{\cdot}CH_2COOH + AgCl$$

Hippuric acid crystallizes from water in rhombic prisms with a slightly bitter taste and an odor resembling that of horse urine. It dissolves in 600 parts of cold water, but readily in hot water and alcohol. It melts at 190° C., and decomposes at 240° C. Boiling with alkalies or dilute acids converts hippuric acid into benzoic acid and glycocoll. Hippuric acid has a strong acid reaction toward litmus. Most metallic oxides dissolve in hippuric acid. The hippurates of the alkalies are exceedingly soluble; their solutions form a cream-colored precipitate with ferric salts, and a white, curdy precipitate with silver nitrate and mercurous nitrate.

SULPHO ACIDS AND DERIVATIVES

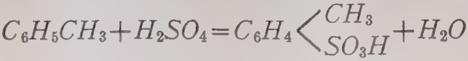
65. Preparation.—The sulpho aromatic acids may be prepared by the direct sulphonation of an aromatic acid or by the sulphonation of a hydrocarbon, such as toluene, and subsequent oxidation of the side chain. By the first method only the meta compound is obtained, the ortho and para varieties being prepared by the second method.

66. Sulphobenzoic Acids, $C_6H_4SO_3H{\cdot}COOH$.—Meta-sulphobenzoic acid is obtained by the direct sulphonation of benzoic acid; thus,

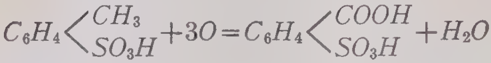


$$C_6H_5COOH + H_2SO_4 = C_6H_4\begin{cases}COOH\\SO_3H\end{cases} + H_2O$$

Ortho and para-sulphobenzoic acids are prepared by sulphonating toluene and then oxidizing the side chain; thus,



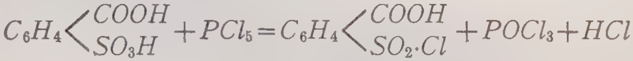
$$C_6H_5CH_3+H_2SO_4=C_6H_4\Big<\begin{array}{l}CH_3\\SO_3H\end{array}+H_2O$$



$$C_6H_4\Big<\begin{array}{l}CH_3\\SO_3H\end{array}+3O=C_6H_4\Big<\begin{array}{l}COOH\\SO_3H\end{array}+H_2O$$

The sulphobenzoic acids are soluble in water and alcohol, and with the exception of the ortho acid are soluble in ether. Of the three acids, ortho-sulphobenzoic acid is the most important because of its use in the synthesis of the sweetening agent known as saccharin.

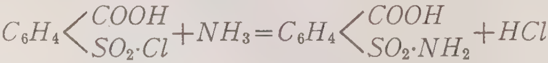
67. Saccharin, $C_6H_4\Big<\begin{array}{l}CO\\SO_2\end{array}\Big>NH$.—Saccharin, or ortho-benzoic sulphinid, may be prepared from ortho-sulphobenzoic acid by the following reactions: Ortho-benzoic sulphon chloride is first formed by the action of phosphorus pentachloride on ortho-sulphonbenzoic acid,



$$C_6H_4\Big<\begin{array}{l}COOH\\SO_3H\end{array}+PCl_5=C_6H_4\Big<\begin{array}{l}COOH\\SO_2{\cdot}Cl\end{array}+POCl_3+HCl$$

ortho-benzoic sulphon chloride

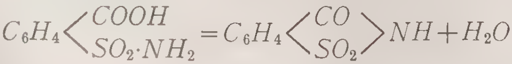
and when ortho-benzoic sulphon chloride is treated with ammonia, ortho-sulphamine benzoic acid is formed,



$$C_6H_4\Big<\begin{array}{l}COOH\\SO_2{\cdot}Cl\end{array}+NH_3=C_6H_4\Big<\begin{array}{l}COOH\\SO_2{\cdot}NH_2\end{array}+HCl$$

ortho-sulphamine benzoic acid

On heating this acid, one molecule of water is lost, with the formation of saccharin,

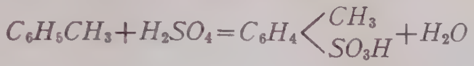


$$C_6H_4\Big<\begin{array}{l}COOH\\SO_2{\cdot}NH_2\end{array}=C_6H_4\Big<\begin{array}{l}CO\\SO_2\end{array}\Big>NH+H_2O$$

saccharin

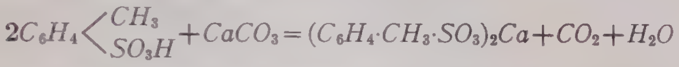
68. The reactions that have been given are not those employed on a manufacturing scale. Commercially, saccharin is made by a number of processes that differ essentially in the methods employed for the preparation of ortho-toluene sulphonamide, an intermediate product.

In one method toluene is heated with fuming sulphuric acid, ortho and para-toluene sulphonic acids being formed,



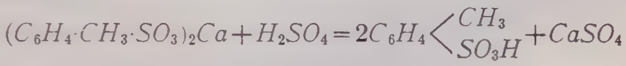
$$C_6H_5CH_3+H_2SO_4=C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H}+H_2O$$

The acids are then converted into their calcium salts by treating them with calcium carbonate,

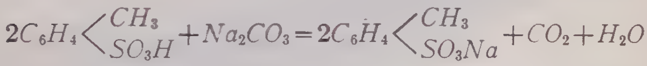


$$2C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H}+CaCO_3=(C_6H_4{\cdot}CH_3{\cdot}SO_3)_2Ca+CO_2+H_2O$$

They are then set free by treatment with sulphuric acid and the sodium salts are formed by the addition of sodium carbonate,

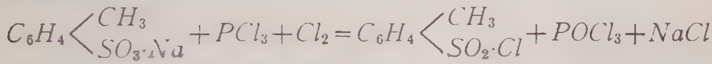


$$(C_6H_4{\cdot}CH_3{\cdot}SO_3)_2Ca+H_2SO_4=2C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H}+CaSO_4$$



$$2C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3H}+Na_2CO_3=2C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3Na}+CO_2+H_2O$$

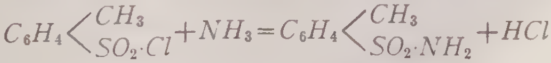
After drying, the sodium salts are treated with phosphorus trichloride and chlorine with the formation of toluene sulphon chloride,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_3{\cdot}Na}+PCl_3+Cl_2=C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_2{\cdot}Cl}+POCl_3+NaCl$$

toluene sulphon
chloride

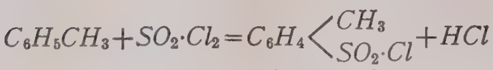
The phosphorus oxychloride is then distilled from the mixture and the residue of ortho and para-toluene sulphon chloride and salt is chilled. Under these conditions the para compound crystallizes and a separation from ortho-toluene sulphon chloride is easily effected. The latter is then treated with ammonia, ortho-toluene sulphonamide being formed,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_2{\cdot}Cl}+NH_3=C_6H_4{<}\genfrac{}{}{0pt}{}{CH_3}{SO_2{\cdot}NH_2}+HCl$$

ortho-toluene
sulphonamide

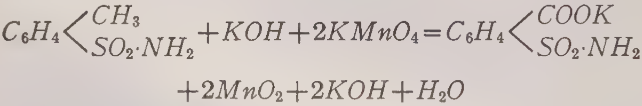
69. In another method for the synthesis of saccharin, the intermediate compound, ortho-toluene sulphonamide, is prepared in a different manner. Thus, toluene is treated with sulphuryl chloride, SO_2Cl_2,



$$C_6H_5CH_3+SO_2\cdot Cl_2=C_6H_4<\begin{array}{l}CH_3\\SO_2\cdot Cl\end{array}+HCl$$

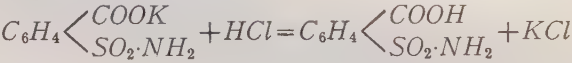
toluene sulphon
chloride

The ortho-toluene sulphon chloride formed is separated from the para compound as already described, and is then treated with ammonia, with the formation of ortho-toluene sulphonamide. From this point both methods make use of the same reactions. Ortho-toluene sulphonamide is oxidized by means of an alkaline solution of potassium permanganate, the potassium salt of ortho-sulphamine benzoic acid being formed; thus,



$$C_6H_4<\begin{array}{l}CH_3\\SO_2\cdot NH_2\end{array}+KOH+2KMnO_4=C_6H_4<\begin{array}{l}COOK\\SO_2\cdot NH_2\end{array}$$
$$+2MnO_2+2KOH+H_2O$$

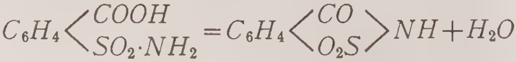
The potassium salt is then treated with hydrochloric acid, ortho-sulphamine benzoic acid being set free,



$$C_6H_4<\begin{array}{l}COOK\\SO_2\cdot NH_2\end{array}+HCl=C_6H_4<\begin{array}{l}COOH\\SO_2\cdot NH_2\end{array}+KCl$$

ortho-sulphamine
benzoic acid

This acid loses water, on heating, with the formation of saccharin,



$$C_6H_4<\begin{array}{l}COOH\\SO_2\cdot NH_2\end{array}=C_6H_4<\begin{array}{l}CO\\O_2S\end{array}>NH+H_2O$$

saccharin

70. Saccharin is a white crystalline substance that melts at 220° C. It is sparingly soluble in cold water but dissolves in hot water and in ether, alcohol, amyl acetate, ethyl acetate, ammonium hydroxide, and in solutions of the alkali carbonates. When dissolved in a solution of sodium bicarbonate, soluble saccharin, or sodium benzosulphinid, is formed. As a sweetening agent saccharin is about five hundred times as efficient as cane sugar. Its use for this purpose in foods is prohibited, however, in the United States and in many other countries. It is used as a substitute for sugar in cases of diabetes.

MONOHYDROXY ACIDS AND DERIVATIVES

71. Methods of Formation.—The monohydroxy acids of the benzene series in which the hydroxyl group is substituted in the ring are known as phenol acids. In some of their properties they resemble both the phenols and the acids. The methods used for the preparation of the first member of the series, hydroxy benzoic acid, are typical and will be used for the purpose of illustration.

1. When sodium phenolate, C_6H_5ONa, is treated with carbon dioxide under pressure, phenyl sodium carbonate, $C_6H_5O{\cdot}COONa$ is formed; thus,

$$C_6H_5ONa+CO_2=C_6H_5O{\cdot}COONa$$

This compound then undergoes molecular rearrangement with the formation of the sodium salt of ortho-hydroxy benzoic acid,

$$C_6H_5O{\cdot}COONa\longrightarrow C_6H_4OH{\cdot}COONa$$

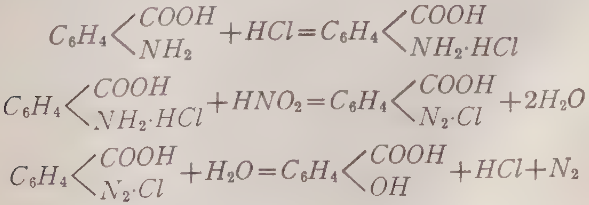
and when the sodium salt is treated with hydrochloric acid, ortho-hydroxy benzoic acid is set free,

$$C_6H_4OH{\cdot}COONa+HCl=C_6H_4OH{\cdot}COOH+NaCl$$

2. When the phenols are boiled with carbon tetrachloride and potassium hydroxide, a mixture of the potassium salts of ortho- and para-hydroxy benzoic acids is formed; thus,

$$C_6H_5OH+CCl_4+5KOH=C_6H_4OH{\cdot}COOK+4KCl+3H_2O$$

3. When ortho-aminobenzoic acid is diazotized and the diazo compound decomposed with water, ortho-hydroxy benzoic acid is formed; thus,



$$C_6H_4{<}\begin{array}{l}COOH\\NH_2\end{array}+HCl=C_6H_4{<}\begin{array}{l}COOH\\NH_2{\cdot}HCl\end{array}$$

$$C_6H_4{<}\begin{array}{l}COOH\\NH_2{\cdot}HCl\end{array}+HNO_2=C_6H_4{<}\begin{array}{l}COOH\\N_2{\cdot}Cl\end{array}+2H_2O$$

$$C_6H_4{<}\begin{array}{l}COOH\\N_2{\cdot}Cl\end{array}+H_2O=C_6H_4{<}\begin{array}{l}COOH\\OH\end{array}+HCl+N_2$$

72. The meta- and para-hydroxy benzoic acids are prepared by methods similar to the foregoing, the only difference being in the starting point. Thus, in the preparation of the acids by the diazo reaction, if benzoic acid is the starting point, on nitration it yields meta-nitrobenzoic acid, which, on reduction, yields meta-aminobenzoic acid; and when this is diazotized and the product decomposed with water, meta-hydroxy benzoic acid is formed. If, however, toluene is the starting point, the product will consist of a mixture of ortho- and para-hydroxy benzoic acids.

73. Salicylic Acid, $C_6H_4OH{\cdot}COOH$.—Salicylic acid, or ortho-hydroxy benzoic acid, is the most important of the hydroxy benzoic acids. It occurs naturally in the buds of the Spiræa ulmaria, and as the methyl ester in the oil of wintergreen from the blossoms of Gaultheria procumbens. It derives its name from salicin, a glucoside in the bark and leaves of the willow. It is prepared by any of the general methods given, although usually by heating dry sodium phenolate with carbon dioxide under pressure.

Salicylic acid is a white, crystalline solid, crystallizing from water in fine needles. It is sparingly soluble in water but is more soluble in hot than in cold water, is soluble in alcohol, and is very soluble in chloroform. It melts at 159° C. and has a sweet, acid taste. Heated carefully, it sublimes, but on rapid heating with soda-lime decomposes into phenol and carbon dioxide:

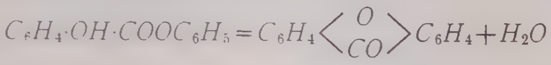
$$C_6H_4{\cdot}OH{\cdot}COOH+2NaOH+CaO$$
$$=C_6H_5OH+Na_2CO_3+Ca(OH)_2$$

Salicylic acid is a powerful antiseptic and is sometimes used as a preservative for foods. Its use in this connection is to be condemned, however, and in many countries its use in foods is prohibited. It is distinguished from its isomerides by its lower melting point and by the violet coloration produced by its aqueous or alcoholic solution when brought in contact with ferric chloride. It is easily separated from meta- and para-hydroxybenzoic acid by boiling with calcium chloride and ammonia, when basic calcium salicylate is precipitated. The sodium salt of salicylic acid is extensively used as a remedy for rheumatism.

74. Phenyl Salicylate, $C_6H_4OH\cdot COOC_6H_5$.—Phenyl salicylate, or salol, is formed when salicylic acid is heated alone to 220° C.; thus,

$$2C_6H_4\cdot OH\cdot COOH = C_6H_4\cdot OH\cdot COOC_6H_5 + H_2O + CO_2$$

It is formed also when salicylic acid, phenol, and phosphorus oxychloride are heated together. When heated, phenyl salicylate changes to xanthone; thus,



$$C_6H_4\cdot OH\cdot COOC_6H_5 = C_6H_4\left\langle\begin{matrix}O\\CO\end{matrix}\right\rangle C_6H_4 + H_2O$$

Salol is a white, crystalline powder with a faint, aromatic odor. It melts at 42° C., is almost insoluble in water, but soluble in alcohol and ether, and is extensively used as an intestinal antiseptic.

75. Acetyl Salicylic Acid, $C_6H_4OOC\cdot CH_3COOH$.—Acetyl salicylic acid, or aspirin, is prepared by heating together at 150° C., under a reflux condenser, 1 part of salicylic acid and 1.5 parts of acetic anhydride. The aspirin thus formed is purified by repeated crystallization until a product that melts at from 133° to 135° C. is obtained. Aspirin is used as a remedy for rheumatism, as a fever reducer, and in general for the relief of pain.

DIHYDROXY AND TRIHYDROXY ACIDS

76. Protocatechuic Acid, $C_6H_3(OH)_2COOH$.—Protocatechuic acid, or 3-4 dihydroxybenzoic acid, is the product of the fusion of caustic potash with many resins, and other organic substances, such as oil of cloves piperic acid, benzoin, asafetida, myrrh, etc. It is prepared synthetically by heating catechol with ammonium carbonate. It crystallizes from water in shining needles of a reddish color, is soluble in alcohol and ether. It decomposes when heated to 199° C. It reduces ammoniacal silver solutions, but has no action on alkaline copper solutions. With ferric chloride, its solutions yield a green coloration, changing, on addition of a very weak solution of sodium carbonate, to blue and finally to red. Distilled with lime, protocatechuic acid is decomposed into pyrocatechol, and carbon dioxide:

$$C_6H_3\cdot(OH)_2\cdot COOH = C_6H_4\cdot(OH)_2 + CO_2$$

77. Gallic Acid, $C_6H_2(OH)_3COOH$.—Gallic acid is probably the best-known trihydroxy acid. It is found in the sumach, in tea, in mangoes, and in many other plants. It is usually prepared by boiling tannin-containing materials with dilute sulphuric acid, or by fusing bromprotocatechuic acid with caustic potash; thus,

$$C_6H_2(OH)_2 \cdot Br \cdot COOH + KOH = C_6H_2(OH)_3 \cdot COOH + KBr$$

It is best prepared, however, by the fermentation of the tannin contained in gall nuts.

Gallic acid crystallizes in fine, silky needles with one molecule of water. It is odorless, and has an astringent, slightly acid taste, and is permanent in the air. It melts at 222° C., and at a slightly higher temperature decomposes into pyrogallol and carbon dioxide. Gallic acid is soluble in 100 parts of cold and three parts of hot water, is readily soluble in ether and sparingly soluble in alcohol.

Alkaline solutions of gallic acid turn brown on exposure to the air. Ferric chloride gives a bluish-black precipitate with gallic acid which is soluble in excess, and gold and silver solutions are reduced by gallic acid.

78. Tannic Acids, or Tannins.—The tannic acids, or tannins, form a large group of organic compounds that are closely related to gallic acid. They differ widely in chemical constitution and reaction, but all have the common property of precipitating gelatine and forming soluble compounds with animal tissue. They are all compounds of carbon, hydrogen, and oxygen, but their ultimate structure is little understood.

When heated, the natural tannins yield catechol, $C_6H_4(OH)_2$, or pyrogallol, $C_6H_3(OH)_3$, and sometimes both. Tannins are commonly divided into two classes; those that yield the whitish deposit on the surface of the leather, called *bloom*, and those that do not. Most tannins that give a bloom to the leather are pyrogallol tannins. The tannins that give no bloom to leather are classed as catechol tannins.

When treated with sulphuric acid, the pyrogallol tannins yield gallic acid or ellagic acid, the latter combining with tannic acid to form the bloom. Under this treatment, the catechol tannins yield the reddish-brown insoluble bodies known to all tanners as *reds*. These reddish-brown insoluble bodies differ from the original tannins in containing fewer molecules of water, and are, therefore, anhydrides of their especial tannic acids.

Hemlock bark yields a series of these reds; the higher members are soluble, precipitate gelatine, and are the principal coloring materials of the bark. The lower members are insoluble at ordinary temperatures and form the sediments found in the tannery vats.

Another method of distinguishing between the pyrogallol and catechol tannins depends on their action with a solution of ferric chloride and with bromine water. Pyrogallol tannins produce a blue-black color with ferric chloride but are not precipitated by bromine water. Catechol tannins produce a green-black color with ferric chloride and are precipitated by bromine water.

79. Leather.—The term leather is applied to the product obtained by the treatment of the hides and skins of animals with certain reagents of vegetable or inorganic origin, that combine with the skin protein and convert the animal tissues into a tough, opaque, pliable, and fibrous substance that is not subject to putrefaction. Raw skins, when wet, are subject to putrefaction, and the operation and action of the vegetable reagents, or tannins, and the inorganic reagents, that cause the changes in the properties of raw skins and hides, is called tanning.

80. Inks.—Gallic acid and the tannins are used in the manufacture of the so-called blue-black inks. The compositions of these inks vary greatly, but most of them contain tannic acid or gallic acid, a ferrous salt, and a soluble blue dye. The solution of the ferrous salt and the acid is not suitable for writing because of its pale green color and consequent lack of visibility, and in order to make the ink immediately visible, the blue dye is added. On exposure to the air, as when the ink is used for writing, gradual oxidation of the ferrous salt takes place with the formation of a black color.

POLYNUCLEAR HYDROCARBONS AND DERIVATIVES

PREPARATION AND PROPERTIES

81. Introductory.—The polynuclear hydrocarbons and their derivatives consist of two or more benzene nuclei, united either directly or by means of a simple aliphatic hydrocarbon group. They are prepared by the same methods as are used in building up the aliphatic hydrocarbons. Thus, ethane may be prepared by treating two molecules of methyl iodide with metallic sodium; and diphenyl, $C_6H_5 \cdot C_6H_5$, is obtained when two molecules of a phenyl halide are treated with metallic sodium.

Theoretically, the number of polynuclear hydrocarbons that might be prepared is large. Actually, however, only a small number are known and only those of importance in industry will be discussed.

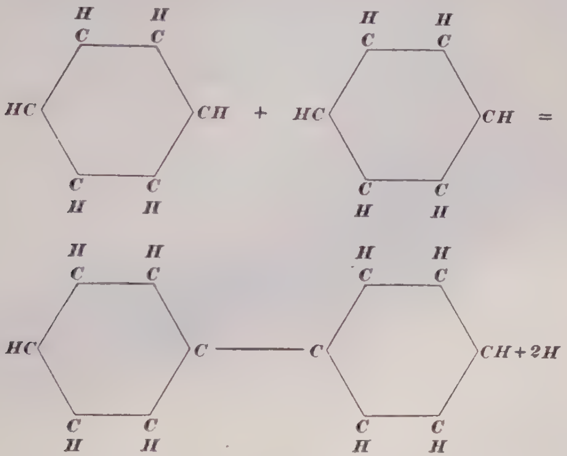
82. Diphenyl, $C_6H_5 \cdot C_6H_5$.—Diphenyl is found in small quantities in the distillate obtained from coal tar. It is formed by passing benzene vapor through a red-hot tube or by treating brombenzene with metallic sodium. In the first reaction, an atom of hydrogen is lost from each molecule of benzene; as in the formulas of Fig. 10.

In the second reaction, sodium bromide is formed along with diphenyl; thus,

$$2C_6H_5Br+2Na=C_6H_5 \cdot C_6H_5+2NaBr$$

Diphenyl is also prepared by heating iodobenzene with powdered copper to 230° C. in a sealed tube. Diphenyl crystallizes in large, colorless plates, melts at 71° C., boils at 254° C., and is easily soluble in hot alcohol and ether. It is very stable and resists the action of ordinary oxidizing agents. It is oxidized to benzoic acid, however, by strong oxidizing agents. In its behavior with the halogens, nitric acid, and sulphuric acid, it resembles benzene.

83. **Benzidine,** $(C_6H_4NH_2)_2$.—Benzidine, dipara-diamino diphenyl, or 4-4 diamino diphenyl is prepared by the reduction of azobenzene in an acid solution. The hydrazobenzene first formed undergoes a rearrangement into benzidine in the presence of the acid; thus,



diphenyl

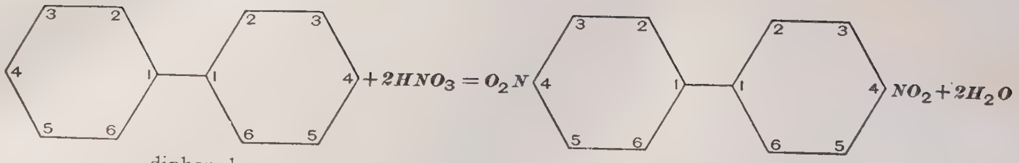
FIG. 10

$$\begin{array}{l} C_6H_5\cdot NH \\ | \\ C_6H_5\cdot NH \end{array} \rightarrow \begin{array}{l} C_6H_4\cdot NH_2 \\ | \\ C_6H_4\cdot NH_2 \end{array}$$

It is also prepared by the reduction of dipara-dinitrodiphenyl. The latter results from the direct nitration of diphenyl when a single nitro group enters each benzene nucleus in the para position, as indicated in Fig. 11.

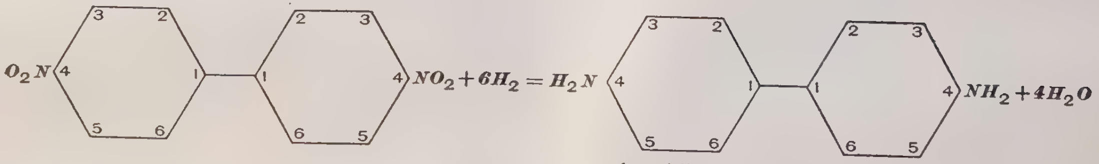
On reduction, benzidine is formed, as indicated in Fig. 12.

Benzidine is a grayish-yellow, crystalline solid soluble in boiling water, alcohol, and ether, and melting at 122° C. It is of considerable technical importance, because many of the azo dyes are obtained from it. Being an amino derivative, benzi-



3
2
4
1
5
6
diphenyl
+2HNO3 = O2N
dipara-dinitro diphenyl
or 4-4 dinitro diphenyl
NO2+2H2O

FIG. 11

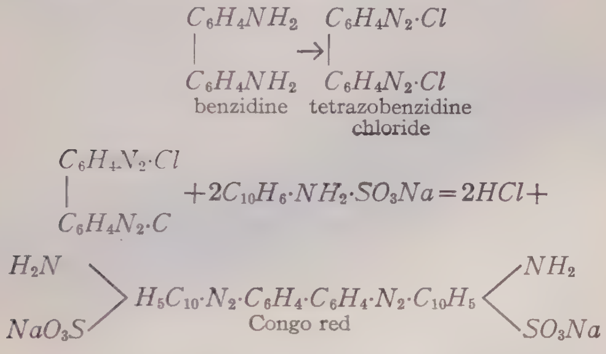


O2N
3
2
4
1
5
6
NO2+6H2 = H2N
benzidine dipara-diamino diphenyl
or 4-4 diamino diphenyl
NH2+4H2O

FIG. 12

dine is easily diazotized, the final product being a compound containing two diazo groups, or a tetrazo compound. This latter compound reacts readily with aromatic amino-sulphonic acids, hydroxy acids, and phenol sulphonic acids, forming dyes that unite directly with cotton.

84. Congo Red.—Congo red is prepared from benzidine by diazotization and subsequent union of the tetrazo compound formed, with sodium naphthionate; thus,



$$\begin{array}{c}C_6H_4NH_2\\ |\\ C_6H_4NH_2\\ \text{benzidine}\end{array} \rightarrow \begin{array}{c}C_6H_4N_2{\cdot}Cl\\ |\\ C_6H_4N_2{\cdot}Cl\\ \text{tetrazobenzidine chloride}\end{array}$$

$$\begin{array}{c}C_6H_4N_2{\cdot}Cl\\ |\\ C_6H_4N_2{\cdot}C\end{array} + 2C_{10}H_6{\cdot}NH_2{\cdot}SO_3Na = 2HCl +$$

$$\begin{array}{c}H_2N\\ NaO_3S\end{array}\Big> \underset{\text{Congo red}}{H_5C_{10}{\cdot}N_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5} \Big< \begin{array}{c}NH_2\\ SO_3Na\end{array}$$

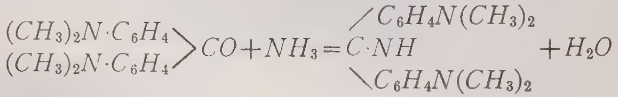
Congo red is obtained as a reddish-brown powder that dissolves in water with the formation of a red solution. It is very sensitive to acids and the aqueous solution turns blue in color when a trace of acid is introduced. Congo red was one of the first dyes to be used for dyeing cotton without previously impregnating the latter with a fixing agent, or mordant, for the dye. Congo red, however, is not fast to light.

85. Diphenyl Methane, $C_6H_5{\cdot}CH_2{\cdot}C_6H_5$.—Diphenyl methane is best prepared by the action of dichlormethane or benzyl chloride on benzene in the presence of anhydrous aluminum chloride (Friedel-Craft reaction); thus,

$$CH_2Cl_2 + 2C_6H_6 = C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + 2HCl$$
$$C_6H_5{\cdot}CH_2Cl + C_6H_6 = C_6H_5{\cdot}CH_2{\cdot}C_6H_5 + HCl$$

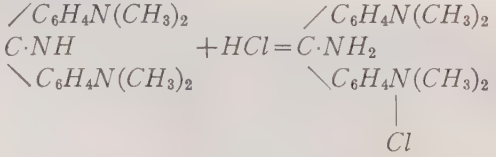
Diphenyl methane is a crystalline solid consisting of long, colorless needles easily soluble in alcohol and ether. It melts at 27° C., boils at 265° C., and has an odor resembling that of oranges. Strong oxidizing agents convert it into diphenyl ketone, or benzophenone.

86. Auramine.—Auramine, a yellow dye related to diphenyl methane, is the hydrochloride of a colorless base obtained by the action of dry ammonia on Michler's ketone. It is prepared by heating a mixture consisting of Michler's ketone, ammonium chloride, and anhydrous zinc chloride. In the reaction that takes place, the ammonium chloride breaks up with the formation of ammonia. The latter then reacts with Michler's ketone to form the colorless, free base of auramine; thus,



$$\left.\begin{matrix}(CH_3)_2N\cdot C_6H_4\\(CH_3)_2N\cdot C_6H_4\end{matrix}\right>CO+NH_3=\begin{matrix}/C_6H_4N(CH_3)_2\\C\cdot NH\\\backslash C_6H_4N(CH_3)_2\end{matrix}+H_2O$$

The water formed as the result of the reaction is removed by the zinc chloride. The dye itself is obtained by the action of hydrochloric acid on the free base; thus,



$$\begin{matrix}/C_6H_4N(CH_3)_2\\C\cdot NH\\\backslash C_6H_4N(CH_3)_2\end{matrix}+HCl=\begin{matrix}/C_6H_4N(CH_3)_2\\C\cdot NH_2\\\backslash C_6H_4N(CH_3)_2\\|\\Cl\end{matrix}$$

Auramine is soluble in hot water (60° to 70° C.), from which, on cooling, it crystallizes in the form of yellow scales that melt at 267° C. Auramine serves as a direct dye for silk and wool; cotton, however, must be mordanted in order to fix the color on the fiber.

87. Mordants.—In the application of coal-tar dyes to animal and vegetable fibers, or to the finished products made from these fibers, it has been found that certain dyes will affix themselves to silk, wool, or cotton when the material is brought in contact with the dyes. On the other hand, certain dyes may be used only on silk or wool and not on cotton unless the fibers of the latter have been treated with what is called a mordant, or mordanting agent. The function of mordants is then to fix dyes on the fiber by converting them into insoluble compounds, the exact constitution of which is unknown. Mordanting agents that are commonly used are tannic acid and the sulphates and acetates of aluminum, chromium, and iron.

88. Triphenylmethane, $CH(C_6H_5)_3$.—Triphenylmethane is obtained by the interaction of benzene and chloroform in the presence of aluminum chloride:

$$CHCl_3+3C_6H_6=CH(C_6H_5)_3+3HCl$$

or by the action of benzene on benzal chloride in the presence of aluminum chloride:

$$C_6H_5 \cdot CHCl_2+2C_6H_6=CH(C_6H_5)_3+2HCl$$

It crystallizes in thin lustrous plates that melt at 92° C., boil at 360° C., and dissolve in hot alcohol and ether, but are insoluble in water. It is a very stable compound. Triphenylmethane is the mother substance of a very important series of dyes. The compound itself is not used in their preparation, but simpler compounds that are converted into its derivatives are used.

TRIPHENYLMETHANE DYES

89. Color and Structure.—Of the various colored compounds that have been treated, not all have the properties of dyes. Thus, by dyes are meant those compounds, derived from coal tar, that have the property of affixing themselves to silk, wool, or cotton fibers from which they cannot be removed by ordinary washing. Certain compounds, such as azobenzene, possess color, but they are not dyes. According to the classification of Witt, compounds of this type are called *chromogens*. Witt has also advanced the theory that the color possessed by a compound is due to the existence in its structure, of certain groups to which he has given the name *chromophore*. Thus, all chromogens or colored compounds and dyes contain a chromophore group. Dyes, however, contain an additional group to which they owe the property of being able to color animal and vegetable fibers more or less permanently. This group has been designated as an *auxochrome* group by Witt.

Azobenzene has been mentioned as a chromogen. The chromophore group that it contains, consists of the azo group, $—N=N—$. Other chromophores are $—C=C—$ and the quinoid group, Fig. 13. Among the auxochrome groups are OH, NH_2, and SO_3H. Thus, when an auxochrome group, such as NH_2, is introduced into azobenzene, aminoazobenzene, a dye, is formed.

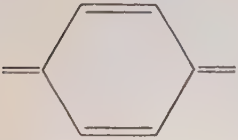
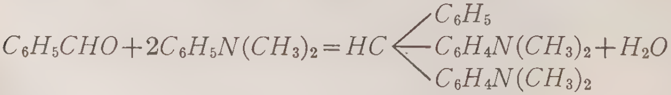


FIG. 13

90. General Reactions.—The formation of a dye of the triphenylmethane series takes place in three steps. In the first step, what is known as the leuco base, is formed. This base is colorless and is an amino derivative of triphenylmethane. In the second step, the color base or carbinol base, a colorless amino derivative of triphenylcarbinol, is formed by oxidation of the leuco base. The third step results in the formation of the dye and consists in warming the color, or carbinol base, with an acid. These steps are well illustrated in the preparation of the dye known as malachite green.

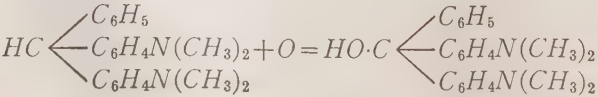
91. Malachite Green.—The leuco base of malachite green is prepared by heating a mixture of benzaldehyde, dimethylaniline, and anhydrous zinc chloride on a water bath. The reaction that takes place may be represented as follows:



$$C_6H_5CHO+2C_6H_5N(CH_3)_2=HC\left\langle\begin{matrix}C_6H_5\\C_6H_4N(CH_3)_2+H_2O\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

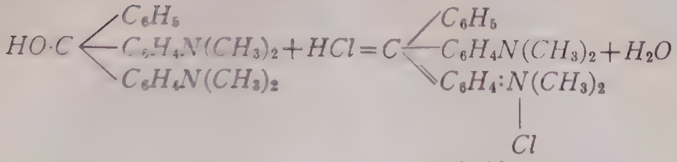
leuco base of malachite green

The colorless leuco base is then oxidized in cold acid solution by means of lead peroxide, the carbinol base being formed, which, on being heated in the acid solution, loses water with the formation of the dye; thus,



$$HC\left\langle\begin{matrix}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.+O=HO\cdot C\left\langle\begin{matrix}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right.$$

carbinol base of malachite green

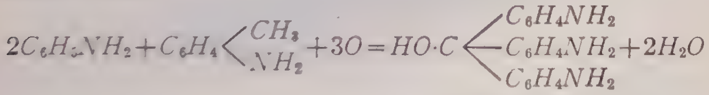


$$HO\cdot C\left<\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{array}\right.+HCl=C\left<\begin{array}{l}C_6H_5\\C_6H_4N(CH_3)_2+H_2O\\C_6H_4{:}N(CH_3)_2\\ \qquad|\\ \qquad Cl\end{array}\right.$$

malachite green dye

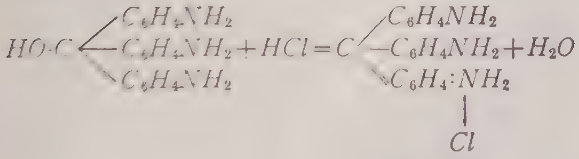
Malachite green is soluble in water and is obtained from its aqueous solution, by the salting out process, in the form of crystals that have a deep-green color. It dyes silk and wool directly, but cotton must be treated with a mordanting agent.

92. Pararosaniline.—Pararosaniline is prepared by oxidizing a mixture of para-toluidine and aniline by means of arsenic acid or nitrobenzene, and then treating with an acid the base formed; thus,



$$2C_6H_5NH_2+C_6H_4\left<\begin{array}{l}CH_3\\NH_2\end{array}\right.+3O=HO\cdot C\left<\begin{array}{l}C_6H_4NH_2\\C_6H_4NH_2+2H_2O\\C_6H_4NH_2\end{array}\right.$$

colorless base
of pararosaniline

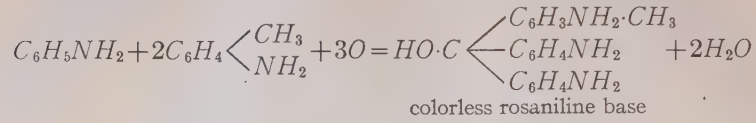


$$HO\cdot C\left<\begin{array}{l}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2\end{array}\right.+HCl=C\left<\begin{array}{l}C_6H_4NH_2\\C_6H_4NH_2+H_2O\\C_6H_4{:}NH_2\\ \qquad|\\ \qquad Cl\end{array}\right.$$

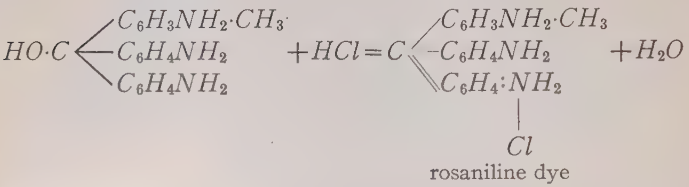
pararosaniline
hydrochloride

Pararosaniline and its salts, which are red dyes, are derivatives of triphenylmethane. They are triaminotriphenylmethane derivatives, however, and therefore differ from malachite green, which is a derivative of diaminotriphenylmethane. Pararosaniline is soluble in water and serves as a direct dye for silk and wool; but cotton must be mordanted.

93. Rosaniline.—Rosaniline, fuchsin, or magenta is prepared by oxidizing a mixture of otho- and para-toluidine and aniline as in the preparation of pararosaniline. The two compounds differ in composition by CH_2. The reactions that take place in the formation of rosaniline may be represented as follows:



$$C_6H_5NH_2+2C_6H_4\left\langle\begin{array}{l}CH_3\\NH_2\end{array}\right.+3O=HO{\cdot}C\left\langle\begin{array}{l}C_6H_3NH_2{\cdot}CH_3\\C_6H_4NH_2\\C_6H_4NH_2\end{array}\right.+2H_2O$$



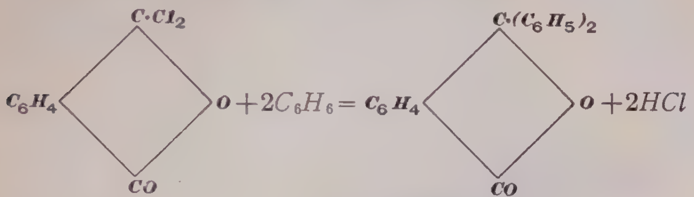
$$HO{\cdot}C\left\langle\begin{array}{l}C_6H_3NH_2{\cdot}CH_3\\C_6H_4NH_2\\C_6H_4NH_2\end{array}\right.+HCl=C\left\langle\begin{array}{l}C_6H_3NH_2{\cdot}CH_3\\C_6H_4NH_2\\C_6H_4{:}NH_2\\ \qquad |\\ \qquad Cl\end{array}\right.+H_2O$$

Rosaniline hydrochloride is a red dye, soluble in water and alcohol, but insoluble in ether. It colors silk and wool a permanent red without the aid of a mordant. Cotton, however, as with other triphenylmethane dyes, must first be mordanted.

94. Derivatives of Pararosaniline and Rosaniline.—Pararosaniline and rosaniline each contain three amino groups in in which the hydrogen atoms are easily replaced by other groups. It is possible, therefore, to obtain a great variety of color shades ranging from red to blue, depending on the number and kind of groups introduced. Thus, methyl violet or pentamethyl pararosaniline, forms metallic, glistening lumps, that are soluble in water and alcohol. Aniline blue, is triphenylrosaniline chloride, made by heating salts of rosaniline with aniline and benzoic acid. Iodine green is a combination of hexamethyl rosaniline with methyl chloride. Aurine is formed by boiling the product obtained by diazotizing pararosaniline, with water, forming trihydroxy-triphenyl carbinol. This is rather unstable and loses one molecule of water, forming aurine. Aurine crystallizes in green needles, which dissolve in alkalies to a red solution. Acid fuchsine, the sulphonic-acid derivative of rosaniline, is prepared by heating rosaniline with strong sulphuric acid to 120° C.

PHTHALEIN DYES

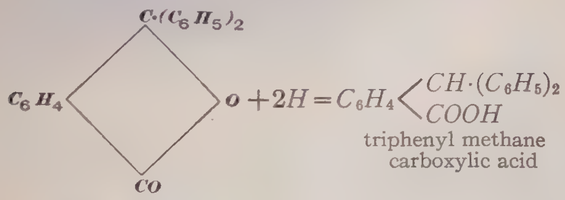
95. Phthalophenone.—Phthalophenone, the simplest phthalein, is not a dye. It is obtained as the result of the reaction that takes place between phthalyl chloride and benzene in the presence of aluminum chloride, thus,



$$C_6H_4\left\langle\begin{matrix}C\cdot Cl_2\\ CO\end{matrix}\right\rangle O+2C_6H_6=C_6H_4\left\langle\begin{matrix}C\cdot(C_6H_5)_2\\ CO\end{matrix}\right\rangle O+2HCl$$

phthalophenone

That the phthaleins are related to triphenylmethane is shown by the formation of triphenylmethanecarboxylic acid when phthalophenone is reduced; thus,

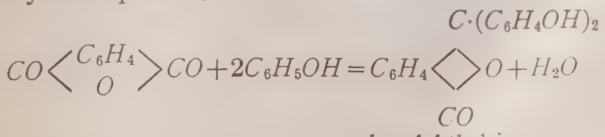


$$C_6H_4\left\langle\begin{matrix}C\cdot(C_6H_5)_2\\ CO\end{matrix}\right\rangle O+2H=C_6H_4\left\langle\begin{matrix}CH\cdot(C_6H_5)_2\\ COOH\end{matrix}\right.$$

triphenyl methane
carboxylic acid

When the acid is distilled with lime, triphenyl methane is obtained.

96. Phenolphthalein.—Phenolphthalein is prepared by heating a mixture of phthalic anhydride, phenol, and a dehydrating agent, such as anhydrous zinc chloride or concentrated sulphuric acid. The reaction that takes place may be represented by the equation,

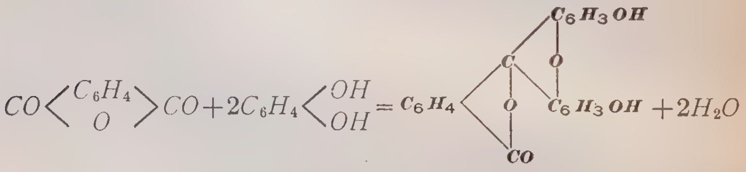


$$CO\left\langle\begin{matrix}C_6H_4\\ O\end{matrix}\right\rangle CO+2C_6H_5OH=C_6H_4\left\langle\begin{matrix}C\cdot(C_6H_4OH)_2\\ CO\end{matrix}\right\rangle O+H_2O$$

phenolphthalein

The formula indicates that phenolphthalein is dihydroxy phthalophenone. Phenolphthalein is most frequently met with in the form of a slightly yellowish powder that melts at from 250° to 253° C. It is only sparingly soluble in hot water and in ether, but is readily soluble in alcohol. When the alcoholic solution is brought in contact with weak solutions of the alkalies, a red color is produced that is dispersed by neutralization, by a slight excess of an acid, or by a strong solution of an alkali. Because of its great sensitiveness to weak acid or alkaline solutions, phenolphthalein is much used as an indicator in volumetric analysis.

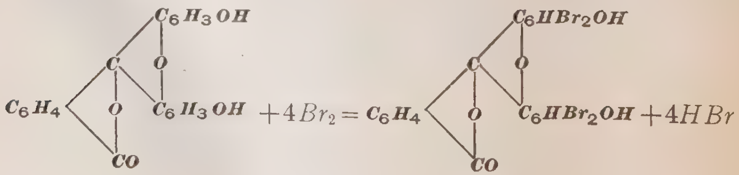
97. Fluorescein.—Fluorescein, or resorcinol phthalein, is obtained by a method analogous to that used in the preparation of phenolphthalein. Thus, when a mixture of phthalic anhydride and resorcinol is heated in the presence of a dehydrating agent, fluorescein is produced.



fluorescein

When the process that involves the foregoing reaction is carried out, fluorescein is obtained as a red powder that is insoluble in water, but that dissolves in alcohol and dilute solutions of the alkalies, with the formation of solutions that show a yellowish-green fluorescence. While fluorescein is a true dye in that it imparts a permanent yellow color to silk and wool, it is not much used as a dye. It is chiefly employed mixed with other colors to impart fluorescence, and in the manufacture of other valuable dyes.

98. Eosin.—Eosin or tetrabromfluorescein is obtained by treating fluorescein with bromine; thus,



eosin

Eosin is only sparingly soluble in water, but dissolves in alcohol, from which it is obtained in the form of red crystals. It dissolves in weak solutions of the alkalies forming solutions that show a green fluorescence. Eosin dyes silk and wool a fluorescent pink shade without the aid of a mordant. The same color is imparted to cotton, which, however, must be mordanted.

DIBENZYL AND DERIVATIVES

99. Dibenzyl, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$.—Dibenzyl, or symmetrical diphenyl ethane, is obtained by the action of sodium on benzyl chloride; thus,

$$2C_6H_5{\cdot}CH_2Cl+2Na=C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5+2NaCl$$

It is obtained also by the action of ethylene chloride on benzene in the presence of aluminum chloride; thus,

$$2C_6H_6+CH_2Cl{\cdot}CH_2Cl=C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5+2HCl$$

Dibenzyl is a solid that melts at 52° C., and boils at 284° C. It is soluble in carbon bisulphide, alcohol, and ether. When oxidized, it yields benzoic acid.

100. Stilbene, $C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5$.—Stilbene, or diphenyl ethylene, is formed by the oxidation of dibenzyl or toluene; thus,

$$C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5+O=C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5+H_2O$$
$$2C_6H_5CH_3+2O=C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5+2H_2O$$

Stilbene melts at from 124° to 125° C. and boils at from 306° to 307° C. It is insoluble in water and sparingly soluble in cold alcohol, but dissolves readily in hot alcohol and in ether. It is of importance in proving the constitution of the coal-tar derivative, phenanthrene.

ORGANIC CHEMISTRY
(PART 7)

CONDENSED-RING HYDROCARBONS

NAPHTHALENE AND ITS DERIVATIVES

NAPHTHALENE

1. Introductory.—In a preceding Section, hydrocarbons that contained two and three distinct benzene nuclei in their structures were treated. Naphthalene, $C_{10}H_8$, and other hydrocarbons, however, which will be taken up subsequently, do not contain individual benzene rings. In them, the benzene molecules are joined in such a manner as to cause each ring to possess carbon atoms in common with the ring to which it is joined. Where this condition exists the benzene rings are said to be condensed and are represented as in the graphic formula for naphthalene, shown in Fig. 1.

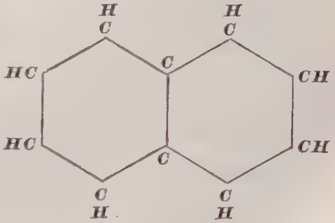


Fig. 1

2. Source, Purification, and Properties of Naphthalene, $C_{10}H_8$.—Naphthalene is present in coal tar to the extent of 5 to 10 per cent. The crude substance is easily obtained from this source in the form of crystals when the fraction of coal tar that boils between 170° C. and 230° C., is allowed to cool. The crude crystalline naphthalene is purified first by

COPYRIGHTED BY INTERNATIONAL TEXTBOOK COMPANY. ALL RIGHTS RESERVED

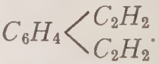
centrifuging or pressing, which removes adhering coal-tar oils, and then treating it with concentrated sulphuric acid, which removes most of the remaining impurities by converting them into sulphonic acids that are soluble in water and nonvolatile and thus may be eliminated by washing, or they are left behind when the purification process consists in distilling the naphthalene with steam or subliming it.

Pure naphthalene is insoluble in water, but dissolves readily in hot alcohol and in ether. It crystallizes in the form of lustrous prisms that melt at 80° C. and boil at 218° C.

Naphthalene possesses a characteristic odor, is volatile below its boiling point, and is very inflammable. It is extensively used as a disinfectant and as an insecticide. The so-called camphor balls or moth balls used as moth repellants consist entirely of naphthalene. It is also used in the manufacture of phthalic acid and lampblack, and for the purpose of increasing the illuminating power of coal gas. In its chemical properties, naphthalene resembles benzene. Thus it reacts with the halogens and nitric and sulphuric acids to form compounds of the same type as the benzene derivatives obtained under similar conditions.

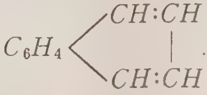
3. Structure of Naphthalene.—The similarity of the behavior of naphthalene and benzene strongly indicates an analogous structure for the two hydrocarbons. Again the readiness with which naphthalene always yields orthophthalic acid on oxidation indicates that it contains a benzene ring in which two side chains have been substituted in the ortho position.

The empirical formula of naphthalene is $C_{10}H_8$ and since it evidently contains a benzene ring in which two hydrogen atoms have been replaced by substituted groups, a structural formula to serve as a starting point toward the accepted formula, may be written,



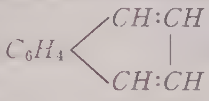
$C_6H_4\left\langle\begin{matrix}C_2H_2\\C_2H_2\end{matrix}\right.$.

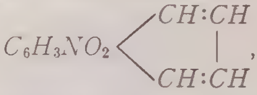
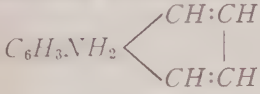
The C_2H_2 groups, however, are unsaturated and to represent this fact the formula may be further developed. Thus,

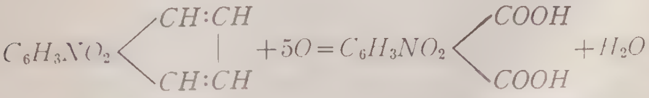


$C_6H_4\left\langle\begin{matrix}CH{:}CH\\ \qquad\;|\\ CH{:}CH\end{matrix}\right.$.

When the

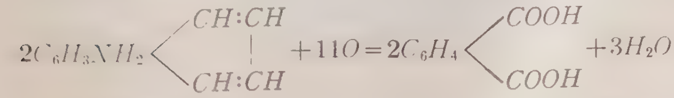
unsaturated aliphatic hydrocarbons were studied, it was shown that they readily unite with the halogens and halogen acids to form addition products. Naphthalene forms addition products with the halogens but the compounds obtained act more like addition products of benzene than those of the unsaturated paraffins. It does not, however, form addition products with the halogen acids and hence it cannot contain unsaturated paraffin radicals as shown by the formula given. This fact renders the formula  $C_6H_4\Big<\begin{array}{l}CH:CH\\ \qquad\ |\\ CH:CH\end{array}$ impossible, but for lack of a better one at this point, it will be used in the discussion that follows.

4. The nature of the groups in naphthalene, which on oxidation are converted into carboxyl groups, as in the formation of ortho-phthalic acid, or that naphthalene really consists of two benzene rings linked together in a peculiar manner, can be shown by means of certain reactions. Thus, when naphthalene is nitrated, nitronaphthalene,  $C_6H_3NO_2\Big<\begin{array}{l}CH:CH\\ \qquad\ |\\ CH:CH\end{array}$, is obtained, and this in turn may be converted to aminonaphthalene,  $C_6H_3NH_2\Big<\begin{array}{l}CH:CH\\ \qquad\ |\\ CH:CH\end{array}$ by reduction of the nitro group. When the two compounds are submitted to the action of oxidizing agents, nitronaphthalene yields nitro-ortho-phthalic acid and aminonaphthalene yields ortho-phthalic acid. Thus,



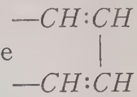
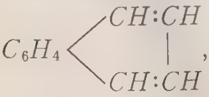
$$C_6H_3NO_2\Big<\begin{array}{l}CH:CH\\ \qquad\ |\\ CH:CH\end{array} + 5O = C_6H_3NO_2\Big<\begin{array}{l}COOH\\ \\ COOH\end{array} + H_2O$$

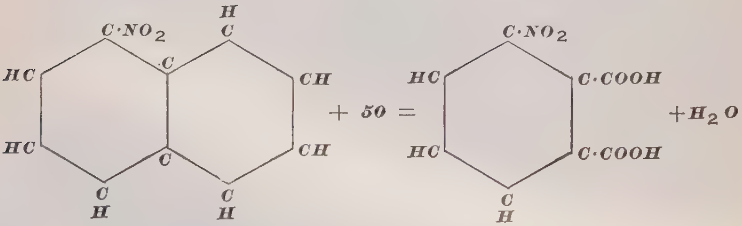
nitronaphthalene nitro-ortho-phthalic acid



$$2C_6H_3NH_2\Big<\begin{array}{l}CH:CH\\ \qquad\ |\\ CH:CH\end{array} + 11O = 2C_6H_4\Big<\begin{array}{l}COOH\\ \\ COOH\end{array} + 3H_2O$$

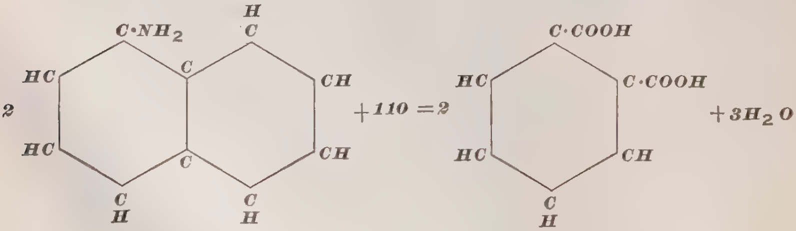
aminonaphthalene ortho-phthalic acid

Since the nitro group substituted in the benzene nucleus of nitronaphthalene appears in nitro-ortho-phthalic acid, it is evident that the benzene nucleus in which the nitro group was substituted has not been affected by the oxidizing reaction and that oxidation has affected only the  $\begin{array}{l}-CH{:}CH\\ \qquad\ |\\ -CH{:}CH\end{array}$ groups. On the other hand, since the NH_2 group of aminonaphthalene, which occupies the same position as the nitro group in nitronaphthalene, and the benzene ring to which it was linked, have been destroyed by the oxidizing reaction that yields ortho-phthalic acid and there yet remains a benzene nucleus in the product, ortho-phthalic acid, it is evident that in naphthalene there are two benzene nuclei and the formula,  $C_6H_4\left\langle\begin{array}{l}CH{:}CH\\ \qquad |\\ CH{:}CH\end{array}\right.$, should be written $C_6H_4{\cdot}C_4H_4$ or as represented in Fig. 1.



nitronaphthalene nitro-ortho-phthalic acid

FIG. 2



aminonaphthalene ortho-phthalic acid

FIG. 3

The oxidation reactions of nitronaphthalene and aminonaphthalene may then be represented as shown in Figs. 2 and 3, respectively.

5. **Isomerism of Naphthalene Derivatives.**—A study of the formula of naphthalene as represented in Fig. 4, will show that two different series of monosubstitution products are theoretically possible. Thus, it is seen that positions *1*, *4*, *5*, and *8*, are alike, that is, each of these positions has the same relation to the rest of the molecule as the other. The second set, however, which consists of the similar positions *2*, *3*, *6*, and *7* are different, in their relation to the rest of the molecule, from the first set. Therefore, substitution of the hydrogen atom at any one of the positions numbered *1*, *4*, *5*, and *8* will give an identical product but one that will differ from that obtained by substitution at any one of the positions numbered *2*, *3*, *6*, and *7*. Substitution products of naphthalene are further distinguished by means of the Greek letters α (alpha) and β (beta) as shown in Fig. 5, in which the carbon and hydrogen atoms have been omitted. Thus, substitution at positions *1*, *4*, *5*, and *8* yields an α derivative, and substitution at positions *2*, *3*, *6*, and *7* yields a β derivative. In the case of a disubstitution product, in which both substituting atoms enter the same nucleus, the prefixes ortho, meta, and para have the same significance as in the case of the disubstitution products of benzene. The position *1-8* or *4-5* is termed the *peri* position.

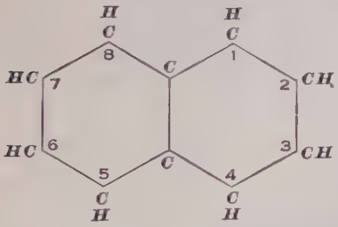


FIG. 4

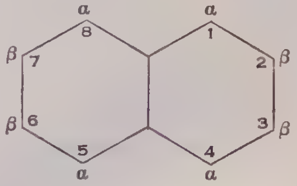


FIG. 5

HOMOLOGUES OF NAPHTHALENE

6. The homologues of naphthalene are prepared by the same methods used for the preparation of the homologues of benzene. Ethyl naphthalene is obtained as the result of the reaction between naphthalene and ethyl iodide in the presence of aluminum chloride. Thus,

$$C_{10}H_8+C_2H_5I=C_{10}H_7{\cdot}C_2H_5+HI$$

Ethyl naphthalene may also be prepared by Fittig's method, which involves the reaction between bromnaphthalene, ethyl bromide, and metallic sodium. Thus,

$$C_{10}H_7Br+C_2H_5Br+2Na=C_{10}H_7{\cdot}C_2H_5+2NaBr$$

The homologues of naphthalene are of little importance. The foregoing reactions are given to emphasize the similarity that exists between the chemical properties of benzene and naphthalene.

HALOGEN NAPHTHALENES

7. The α-halogen substitution products of naphthalene may be obtained by treating naphthalene at its boiling point, with chlorine or bromine. Both α- and β-compounds are obtained by treating naphthalene sulphonic chloride with phosphorus pentachloride or phosphorus pentabromide; thus,

$$C_{10}H_7{\cdot}SO_2Cl+PCl_5=C_{10}H_7Cl+POCl_3+SO_2Cl_2$$

They may also be prepared by diazotizing α- or β-naphthylamine and then decomposing the diazo compound formed.

α-bromnaphthalene is a liquid above 6° C. It boils at 279° C.

β-bromnaphthalene is a solid that melts at 59° C., and boils at 281° C. The α- and β-bromnaphthalenes are soluble in benzene, alcohol, and ether.

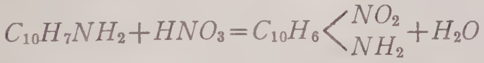
α-chlornaphthalene is a liquid that boils at 263° C. β-chlornaphthalene is a solid that melts at 56° C. and boils at 265° C. Both chlorine derivatives are insoluble in water, but dissolve in alcohol and ether.

Of the halogen addition products of naphthalene, the tetrachloride, $C_{10}H_4Cl_4$, is the most important. It is prepared at ordinary temperatures by treating napthalene with chlorine. When subjected to the action of oxidizing agents, naphthalene tetrachloride yields orthophthalic acid.

NITRONAPHTHALENES

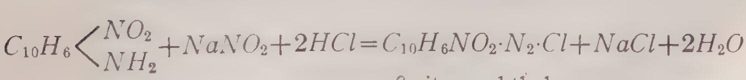
8. α-Nitronaphthalene, $C_{10}H_7NO_2$.—α-Nitronaphthalene is obtained by the direct nitration of naphthalene, the process being much the same as that used in the nitration of benzene. β-Nitronaphthalene is a solid compound that melts at 61° C. and boils at 304° C. It is insoluble in water, but dissolves in alcohol and in ether.

9. β-Nitronaphthalene, $C_{10}H_7NO_2$.—β-Nitronaphthalene is not obtained by the direct nitration of naphthalene. It is obtained indirectly from α-naphthylamine by treating the latter with dilute nitric acid, β-nitro-α-naphthylamine being formed. This compound is then diazotized in an alcoholic solution, and, when finely divided cuprous oxide is added to the solution of the diazo compound and the mixture warmed, nitrogen is evolved and β-nitronaphthalene is formed. The reactions that take place may be represented as follows:



$$C_{10}H_7NH_2+HNO_3=C_{10}H_6\Big<\begin{matrix}NO_2\\NH_2\end{matrix}+H_2O$$

α-naphthylamine β-nitro-α-naphthylamine



$$C_{10}H_6\Big<\begin{matrix}NO_2\\NH_2\end{matrix}+NaNO_2+2HCl=C_{10}H_6NO_2\cdot N_2\cdot Cl+NaCl+2H_2O$$

β-nitronaphthalene diazonium chloride

$$2C_{10}H_6NO_2\cdot N_2\cdot Cl+Cu_2O+C_2H_5OH$$
$$=2C_{10}H_7NO_2+2CuCl+2N_2+CH_3COOH$$

β-nitronaphthalene

β-nitronaphthalene is a solid that melts at 79° C. It is insoluble in water but is very soluble in alcohol and in ether.

AMINONAPHTHALENES OR NAPHTHYLAMINES

10. α-Naphthylamine, $C_{10}H_7NH_2$.—α-Naphthylamine is obtained by reducing α-nitronaphthalene with nascent hydrogen. It is a solid compound that melts at 50° C. and boils at 301° C. It is sparingly soluble in water but dissolves readily in alcohol and in ether. Its salts give a blue precipitate with ferric chloride solution.

11. β-Naphthylamine, $C_{10}H_7NH_2$.—β-Naphthylamine may be obtained by the reduction of the corresponding nitronaphthalene. It is more readily obtained, however, by heating β-naphthol with ammonio-zinc chloride or ammonio-calcium chloride, which are prepared by passing ammonia over anhydrous zinc chloride or anhydrous calcium chloride. On heating, these reagents break up into ammonia and the anhydrous salt. The action of ammonia on β-naphthol at about 250° C., may be represented by the equation,

$$C_{10}H_7OH+NH_3=C_{10}H_7NH_2+H_2O$$

β-Naphthylamine melts at 112° C. It is soluble in water and in alcohol. It is distinguished from α-naphthylamine by the fact that its salts do not produce a color or a precipitate with ferric chloride solution.

NAPHTHALENE SULPHONIC ACIDS

12. Both α-naphthalene sulphonic acid and β-naphthalene sulphonic acid are obtained by heating naphthalene with strong sulphuric acid. If the reaction is carried out at 80° C., the product consists largely of the α-compound. At 160° C., however, the β-compound is formed.

The properties of the naphthalene monosulphonic acids are practically the same as those of the corresponding benzene derivatives. Thus, they and their salts are soluble in water. On fusion of the acids with the caustic alkalies, they yield hydroxy derivatives of naphthalene, or naphthols. When fused with potassium cyanide they yield cyanides or nitriles.

NAPHTHOLS

13. As has been stated, the naphthols are prepared by fusion of the naphthalene sulphonic acids with the caustic alkalies. In many respects the properties of the naphthols resemble those of the phenols. The hydroxy group, however, is more easily replaced in the former than in the latter.

α-Naphthol crystallizes in shining needles with the odor of phenol; it has a disagreeable taste. It is slightly soluble in water, readily soluble in alcohol and in ether, melts at 94° C., and boils at 280° C.

β-Naphthol forms colorless, crystalline laminæ soluble in alcohol, ether, oils, alkaline liquids, and in water. It melts at 122° C. and boils at 286° C.

Ferric chloride yields a flocculent, violet precipitate with α-naphthol, and with β-naphthol it gives a greenish coloration and a precipitate of β-dinaphthol.

NAPHTHYLAMINE SULPHONIC ACID

14. Naphthionic acid, $C_{10}H_6NH_2SO_3H$, or 1-4 naphthylamine sulphonic acid, is of importance because of its application in the manufacture of azo dyes from naphthalene and its derivatives. Naphthionic acid is prepared by heating α-naphthylamine with sulphuric acid. It is a crystalline compound that is only sparingly soluble in such solvents as water, alcohol, and ether.

NAPHTHALENE DYES

15. Martius Yellow.—Martius yellow, which is the sodium or potassium salt of dinitro-α-naphthol, is prepared by nitrating α-naphthol and then neutralizing with sodium carbonate, the dinitro-α-naphthol being formed; thus,

$$C_{10}H_7OH + 2HNO_3 = C_{10}H_5(NO_2)_2OH + 2H_2O$$
$$2C_{10}H_5(NO_2)_2OH + Na_2CO_3 = 2C_{10}H_5(NO_2)_2ONa + CO_2 + H_2O$$

Martius yellow appears on the market as an orange-yellow powder that is soluble in water. Wool and silk are colored a golden-yellow shade by the dye.

16. Naphthol Yellow S.—In the preparation of naphthol yellow S, α-naphthol trisulphonic acid is first formed by the action of hot concentrated sulphuric acid on α-naphthol; thus,

$$C_{10}H_7OH+3H_2SO_4=C_{10}H_4(SO_3H)_3OH+3H_2O$$

This compound is then nitrated, two of the sulphonic acid groups being replaced by nitro groups; thus,

$$C_{10}H_4(SO_3H)_3OH+2HNO_3=C_{10}H_4(NO_2)_2\cdot SO_3H\cdot OH+2H_2SO_4$$

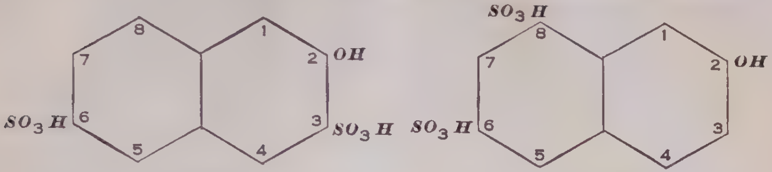
Naphthol yellow S is the sodium salt of the acid formed by the foregoing reaction. It appears as a bright-yellow or orange-colored powder that dissolves readily in water. In an acid bath it dyes wool and silk a yellow color. It is sometimes adulterated by admixture with the cheaper Martius yellow.

17. Naphthalene Azo Dyes.—When the azo dyes were discussed in a preceding Section, only those were considered which resulted from the linking or coupling of the diazo compound with another benzene derivative such as dimethyl aniline. In the present case, the diazo compound is coupled with a naphthalene derivative, which gives rise to an entirely different type of dye.

18. R-Acid and G-Acid.—R-acid, or 2-naphthol-3-6 disulphonic acid, and G-acid or 2-naphthol-6-8-disulphonic acid are two important naphthalene derivatives used in the manufacture of a series of colors that range from yellow to scarlet in shade and which are called Ponceau or Bordeaux dyes. R-acid derives its name from the fact that it is used in making red dyes. G-acid is used in the manufacture of yellow dyes and takes its name from the first letter of the German word, *gelb*, meaning yellow.

Both acids are obtained when β-naphthol is heated with concentrated sulphuric acid, during a period of several hours, at about 105° C. By this method the yield of R-acid exceeds that of G-acid and a separation is effected by adding a solution of sodium chloride to the reaction mixture. This causes the sodium salt of R-acid, or R-salt as it is called, to crystallize, while the G-salt formed remains in solution.

The method employed to obtain the greatest possible yield of G-salt varies from the foregoing in that a larger quantity of sulphuric acid and a lower temperature is used, and the period of reaction is much longer.

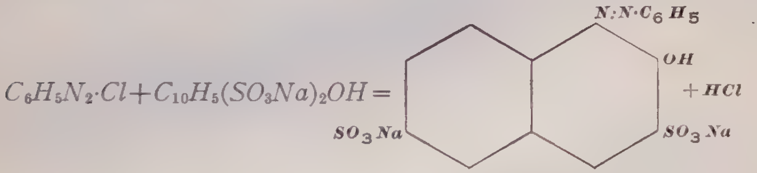


R-Acid
2-naphthol-3-6-disulphonic acid

G-Acid
2-naphthol-6-8-disulphonic acid

FIG. 6

The structural formulas for R-acid and G-acid are written as shown in Fig. 6.



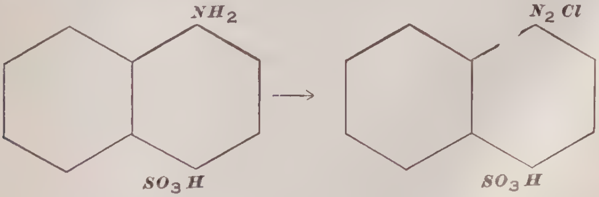
$C_6H_5N_2 \cdot Cl + C_{10}H_5(SO_3Na)_2OH =$

Ponceau 2G

FIG. 7

19. Ponceau 2G.—Ponceau 2G, a scarlet dye, is made by coupling diazobenzene chloride with R-salt, as indicated in Fig. 7.

The dye appears as a red powder, which is soluble in water. In an acid bath, wool and silk are colored a reddish orange by the dye.



naphthionic acid

diazotized naphthionic acid

FIG. 8

20. Bordeaux S.—Bordeaux S results from the coupling of diazotized naphthionic acid with R-acid, the formulas of which are shown in Fig. 8, and subsequent salting out of the dye. The reaction that takes place is represented by the equation shown in Fig. 9.

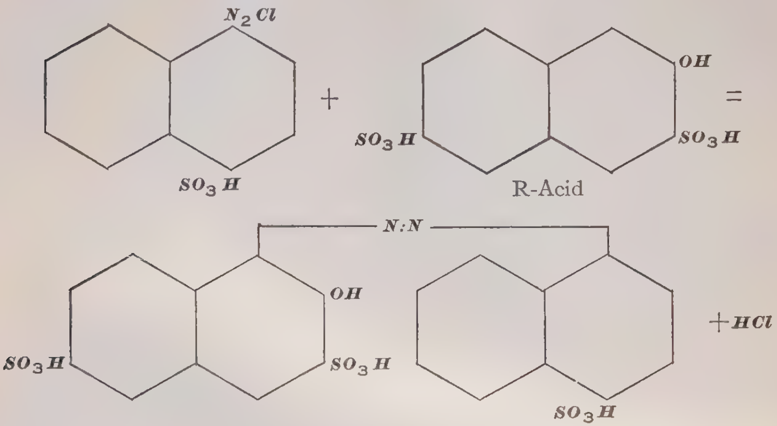
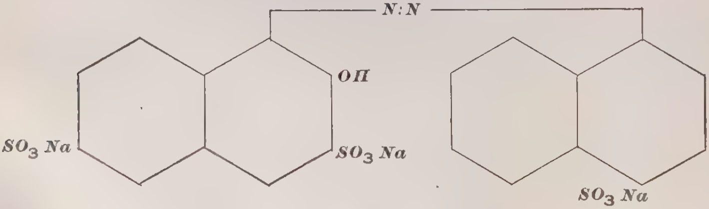


FIG. 9

The sodium salt of the acid or Bordeaux S has the formula shown in Fig. 10.



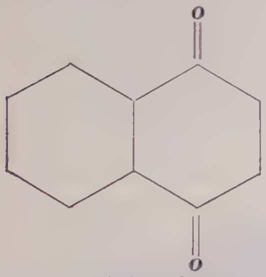
Bordeaux S
FIG. 10

Bordeaux S colors wool and silk a bluish red in an acid bath. The dye is fast to light and is not affected by acids or alkalies.

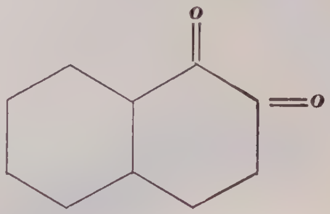
NAPHTHAQUINONES

21. **α-Naphthaquinone,** $C_{10}H_6O_2$.—When certain disubstitution products of naphthalene are oxidized, or when naphthalene itself is subjected to the action of oxidizing agents, compounds known as naphthaquinones are obtained.

α-Naphthaquinone may be prepared by oxidizing 1-4 diaminonaphthalene, 1-4 aminonaphthol or naphthalene. It is a crystalline compound that melts at 125° C. It is yellow in color, is volatile, and possesses a strong odor. α-Naphthaquinone is sparingly soluble in water but dissolves readily in alcohol and in ether. Its structure is represented by the formula shown in Fig. 11.



α-naphthaquinone
FIG. 11



β-naphthaquinone
FIG. 12

22. β-Naphthaquinone, $C_{10}H_6O_2$.—β-Naphthaquinone may be obtained by oxidizing β-amino-α-naphthol. It is a red crystalline compound that is odorless and non-volatile. It melts at 115° to 120° C., with decomposition and is soluble in water and alcohol. The structure of β-naphthaquinone is represented by the formula of Fig. 12.

On oxidation, both naphthaquinones yield ortho-phthalic acid.

ANTHRACENE AND ITS DERIVATIVES

ANTHRACENE

23. Occurrence, Recovery, and Purification.—Anthracene, $C_{14}H_{10}$, occurs to the extent of less than 5 per cent. in the coal tar distillate known as anthracene oil, which boils above 370° C. A product known as 50-per-cent. anthracene is recovered from this distillate, along with impurities, such as phenanthrene, an isomer of anthracene, and carbazole, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!\!>NH$, by fractional distillation. Practically pure anthracene may be obtained by distilling the 50-per-cent. product in iron retorts with caustic potash or potassium carbonate. In this way, potassium carbazole, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>NK$, which is non-volatile, is formed The distillate contains anthracene and phenanthrene. The latter is removed by washing the mixture with carbon bisulphide, phenanthrene being more soluble in this solvent than is anthracene. The product thus obtained still contains traces of impurities and is further purified by crystallization from benzene followed by distillation with steam.

Anthracene is used extensively in the commercial manufacture of the dye known as alizarin.

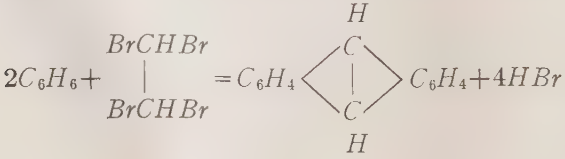
24. Properties of Anthracene.—Anthracene crystallizes in colorless, lustrous leaflets that possess a fine blue fluorescence. It is easily soluble in benzene, difficultly soluble in alcohol and in ether, melts at 213° C., and boils at 351° C. In its chemical properties, anthracene resembles benzene and naphthalene. Thus, it forms substitution and addition products with the halogens and yields sulphonic acids with sulphuric acids. It does not, however, form a nitro compound with nitric acid but is oxidized by this and other oxidizing agents to anthraquinone, $C_6H_4(CO)_2C_6H_4$.

25. Structure of Anthracene.—The probable structure of anthracene can be shown best by the reactions involved in the methods employed for its synthetic preparation.

When a mixture of metallic sodium and ortho-brombenzyl bromide is heated, anthracene is obtained; thus,

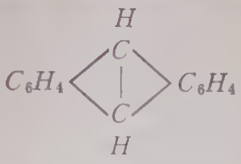
$$2C_6H_4Br{\cdot}CH_2Br+4Na=(C_6H_4{\cdot}CH)_2+4NaBr+H_2$$

It is also formed by the reaction that takes place between benzene and acetylene tetrabromide; thus,



$$2C_6H_6+\begin{matrix}BrCHBr\\|\\BrCHBr\end{matrix}=C_6H_4\left<\begin{matrix}H\\C\\|\\C\\H\end{matrix}\right>C_6H_4+4HBr$$

These syntheses indicate that anthracene consists of two phenylene groups united by a C_2H_2 group; thus,



and consequently it may be represented by the condensed ring formula, shown in Fig. 13.

26. Isomerism of Anthracene Derivatives.—A study of the condensed ring formula for anthracene indicates that three classes of monosubstitution products are possible, namely α, β, and γ derivatives. The positions *1*, *4*, *5*, and *8* are alike and substituents in these positions form the α derivatives; the positions *2*, *3*, *6*, and *7*, are alike also and in these positions β derivatives are formed; while in positions *9* and *10* substituents yield the γ products.

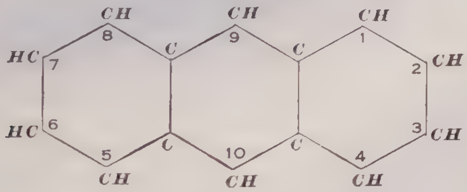


FIG. 13

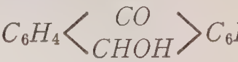
27. Anthraquinone, $C_6H_4(CO)_2C_6H_4$.—Anthraquinone is the most important of the many derivatives of anthracene. It is a diketone obtained by the direct oxidation of anthracene by nitric or chromic acids:

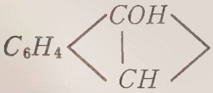
$$C_{14}H_{10}+3O=C_{14}H_8O_2+H_2O$$

or by the distillation of calcium benzoate or calcium phthalate.

It is formed also by the interaction of phthalic anhydride and benzene in the presence of dehydrating agents. This also establishes the structure of anthraquinone to be the same as anthracene with the *CH* groups *9* and *10* replaced by the *CO* groups. A further proof of the correctness of this formula is that the formula indicates only two isomeric monosubstitution products, and experiment has verified this.

On a commercial scale, anthraquinone of the highest possible purity is made by oxidizing 50-per-cent. anthracene in lead-lined tanks, with potassium bichromate and sulphuric acid. The anthraquinone separates from the reaction mixture in the form of a powder and is freed from acid by repeated washing with water. To effect further purification the product thus obtained, is dried, then dissolved in concentrated sulphuric acid and reprecipitated by the addition of water. It is then distilled in a current of steam.

28. Properties of Anthraquinone.—Anthraquinone crystallizes from acetic acid in yellow needles melting at 285° C. and boiling at 380° C. It sublimes before boiling, forming long, yellow prisms. It is insoluble in water but slightly soluble in alcohol and in ether. Anthraquinone is very stable, oxidizing agents having very little effect on it. It is used as the starting point in the manufacture of the alizarin dyes. Contrary to expectation, anthraquinone is not a true quinone but has more the character of a diketone. Fused with caustic potash is yields benzoic acid. Reducing agents convert it successively into *oxanthranol*,  $C_6H_4\left\langle\begin{array}{c}CO\\CHOH\end{array}\right\rangle C_6H_4$, *anthranol*,



$$C_6H_4\left\langle\begin{array}{c}COH\\|\\CH\end{array}\right\rangle C_6H_4$$, and *anthracene.*

29. Alizarin, $C_{14}H_6(OH)_2O_2$.—Alizarin or dihydroxy anthraquinone is the most important derivative of anthracene. It was originally obtained from the root of the madder (Rubia tinctorum), a plant that is a native of southern Europe, and in which it exists as ruberythric acid, a glucoside of alizarin. When the glucoside is boiled with dilute acids or when it is subjected to fermentation, it undergoes hydrolysis with the formation of alizarin and dextrose; thus,

$$\underset{\text{ruberythric acid}}{C_{26}H_{28}O_{14}}+2H_2O=C_{14}H_6(OH)_2O_2+\underset{\text{dextrose}}{2C_6H_{12}O_6}$$

30. Synthesis of Alizarin.—Alizarin was first synthetically prepared by Graebe and Libermann, who, by reducing the natural product by heating it with zinc dust, obtained a product that proved to be anthracene. This result together with the results obtained in their researches on quinone, led Graebe and Liebermann to assume that alizarin was the dihydroxy quinone of anthracene, or dihydroxy anthraquinone. The relationship existing between anthracene, anthraquinone and alizarin is shown by the formulas,

$C_{14}H_{10}$	$C_{14}H_8O_2$	$C_{14}H_8O_4$
anthracene	anthraquinone	alizarin

To verify their conclusions, Graebe and Liebermann attempted to prepare alizarin from anthraquinone by brominating the latter and then fusing the dibromanthraquinone thus formed with caustic potash. Their efforts were attended by success and the problem of synthetically preparing a vegetable dye was solved for the first time. The reactions involved by the use of this method may be represented as follows:

$$C_{14}H_8O_2+2Br_2=C_{14}H_6Br_2O_2+2HBr$$

$$C_{14}H_6Br_2O_2+2KOH=C_{14}H_6(OH)_2O_2+2KBr$$

The foregoing process of Graebe and Liebermann could not be employed on a manufacturing scale, however, because the expense connected with the use and recovery of bromine would not permit the artificial alizarin, produced by its use, to compete with the product obtained from natural sources.

31. Commercial Manufacture of Alizarin.—Work on the development of a more economical process was then carried on simultaneously by Perkin in England and by Graebe and Liebermann in Germany and the process finally developed by these investigators, who worked independently, involved practically the same reactions and is essentially the process used today.

In the commercial process practically pure anthraquinone is heated with fuming sulphuric acid at 160° C., and is converted into the monosulphonic acid of anthraquinone. The sodium salt of this acid is then mixed with caustic soda and potassium chlorate, which acts as an oxidizing agent, and the mixture is heated under pressure for several days at a temperature ranging from 180° to 200° C. The reaction mixture is then dissolved in water and the alizarin set free from its sodium salt by the addition of hydrochloric acid. The yellow, crystalline precipitate thus obtained is filtered, washed free from acid with water, and is then sold in the form of 20-per-cent. paste.

The reactions involved in the commercial process may be represented by the following equations:

$$\underset{\text{anthraquinone}}{C_6H_4(CO)_2C_6H_4}+H_2SO_4=\underset{\substack{\text{anthraquinone}\\\text{monosulphonic acid}}}{C_6H_4(CO)_2C_6H_3\cdot HSO_3}+H_2O$$

$$C_6H_4(CO)_2C_6H_3\cdot HSO_3+NaOH=\underset{\text{sodium salt}}{C_6H_4(CO)_2C_6H_3\cdot NaSO_3}+H_2O$$

$$\begin{aligned}&C_6H_4(CO)_2C_6H_3\cdot NaSO_3+3NaOH+O\\&=\underset{\text{sodium salt of alizarin}}{C_6H_4(CO)_2C_6H_2\cdot(ONa)_2}+2H_2O+Na_2SO_3\end{aligned}$$

$$C_6H_4(CO)_2C_6H_2\cdot(ONa)+2HCl=\underset{\text{alizarin}}{C_6H_4(CO)_2C_6H_2(OH)_2}+2NaCl$$

32. Properties of Alizarin.—Alizarin crystallizes in the form of red needles that melt at 289 to 290° C. and boil at 430° C. It is almost insoluble in water but dissolves readily in alcohol, ether, carbon bisulphide, and in solutions of the caustic alkalies. Distilled with zinc dust, it is converted into anthracene, this reaction giving the first clue to the constitution of alizarin.

The value of alizarin as a dye depends on its power to form with metallic oxides fine-colored, insoluble compounds, or *lakes*. Dissolved in alkalies, a compound of a purple-red color is formed; calcium and barium oxides produce a compound of a blue color; aluminum and tin oxides produce compounds of various shades of red; ferric oxide produces a violet-black compound, and chromium a claret-colored compound.

33. Structure of Alizarin.—The formation of alizarin from anthraquinone proves it to be a derivative of the latter substance, and the formation of alizarin, by heating phthalic anhydride with sulphuric acid and catechol proves that both the hydroxyl groups are in the same nucleus. Since the hydroxyl groups in catechol occupy the ortho position, the same must be true of alizarin. Hence, alizarin must have one of the structural formulas given in Fig. 14.

When alizarin is subjected to nitration two mononitro derivatives are obtained, each with the nitro group in the same nucleus as the hydroxyl groups, since both can be oxidized to phthalic acid. The first formula alone admits of such formation, hence the hydroxyl groups of alizarin must be in the α and β positions.

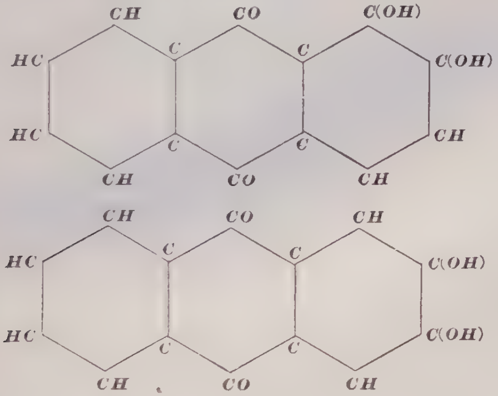


FIG. 14

34. Purpurin, $C_{14}H_5(OH)_3O_2$.—Purpurin, or trithydroxyanthraquinone, is found with alizarin in madder root. It can be prepared synthethically by heating alizarin with manganese dioxide and sulphuric acid. It can be prepared also by melting tribromanthraquinone with caustic potash. It is separated from natural alizarin by boiling with alum, which dissolves the purpurin only.

Purpurin crystallizes in orange-colored needles slightly soluble in water and soluble in alcohol and ether. It melts at 253° C., and sublimes in red needles. Its solutions have a pure red color. Calcium and barium oxides form a purple-red precipitate, and aluminum oxide a beautiful scarlet.

Two isomerides of purpurin, *flavopurpurin* and *anthrapurpurin*, are found in artificial alizarin. Flavopurpurin crystallizes in golden needles soluble in alcohol. Anthrapurpurin closely resembles alizarin, but fuses at a higher temperature, and is more soluble in water. Its metallic salts are more brilliant in color than those of alizarin, so that their presence in alizarin is really an advantage.

PHENANTHRENE

35. Phenanthrene, $C_{14}H_{10}$, an isomeride of anthracene, is also found in the higher-boiling fractions of the distillate obtained from coal tar. It is separated from anthracene by treating the mixture of the two with carbon bisulphide, which dissolves the phenanthrene. It may be formed by passing the vapors of dibenzyl through red-hot tubes. On oxidation with chromic acid, it yields phenanthraquinone and diphenic acid. The conversion of phenanthrene into diphenic acid shows that it is a derivative of diphenyl and is made up of three condensed benzene rings.

TERPENES

SOURCE, GENERAL PROPERTIES, AND CLASSIFICATIONS

36. Source.—The terpenes are hydrocarbons that occur in the oils derived from certain types of plant life. These oils are known as essential, volatile or ethereal oils and are obtained by one of the following processes: Distillation of parts of the plant, such as the root, bark, leaves or fruit; distillation of exuded resins, as in the case of oil of turpentine; by expression of the oil from some part of the plant, as in the case of the oils of lemon and orange; by extraction with solvents. The essential oils are usually liquids at ordinary temperatures; they possess well-defined odors and in most cases can be distilled with little or no decomposition. They constitute an abundant source of terpenes and some of them are extensively used in the preparation of perfumes. The terpenes are usually obtained from this source by distillation of the oil with steam. The names of the commoner essential oils, together with their chief constituents, are given in Table I.

TABLE I

ESSENTIAL OILS

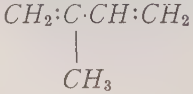
Name of Oil	Names and Formulas of Chief Constituents
Allspice	Eugenol, $C_2H_5 \cdot C_6H_3 \cdot OH \cdot OCH_3$.
Anise	Anethol, $CH_3 \cdot CH \cdot CH \cdot C_6H_4 \cdot OCH_3$; safrol, $C_3H_5 \cdot C_6H_3 \cdot O_2 \cdot CH_2$; eugenol.
Bergamot	Linalyl acetate, $C_{10}H_{17}COOCH_3$; linalol, $C_{10}H_{17}OH$; limonene, $C_{10}H_{16}$.
Bitter almond	Benzaldehyde, hydrocyanic acid.
Camphor	Dipentene, $C_{10}H_{16}$; camphor, $C_{10}H_{16}O$; phellandrene, $C_{10}H_{16}$; pinene, $C_{10}H_{16}$; eugenol; safrol.
Caraway	Limonene; carvone, $C_{10}H_{14}O$.
Clove	Eugenol.
Eucalyptus	Phellandrene; cineol, $C_{10}H_{18}O$.
Fennel	Anethol; fenchone, $C_{10}H_{16}O$.
Geranium	Geraniol, $C_9H_{15}CH_2OH$; citronellol, $C_{10}H_{20}O$.
Jasmine	Benzyl acetate; linalyl acetate; linalol.
Lavender	Pinene, camphene, $C_{10}H_{16}$, cineol; camphor; borneol, $C_{10}H_{17}OH$; linalol.
Lemon	Limonene; citral, $C_9H_{15}CHO$.
Nutmeg	Pinene.
Orange	Limonene.
Pennyroyal	Pulegone, $C_{10}H_{16}O$.
Peppermint	Menthol, $C_{10}H_{19}OH$; menthone, $C_{10}H_{18}O$; pinene; cineol; limonene.
Rosemary	Pinene, camphene; cineol; camphor; borneol.
Sassafras	Safrol; eugenol; camphor; pinene; phellandrene.
Spearmint	Carvone, $C_{10}H_{14}O$; limonene; pinene.
Thyme	Thymol, $(CH_3)_2CH \cdot C_6H_3(CH_3)OH$; carvacrol, $(CH_3)_2CH \cdot C_6H_3(CH_3)OH$; cymeme; linalol; borneol.
Turpentine	Pinene; sylvestrene, $C_{10}H_{16}$; dipentene.
Wintergreen	Methyl salicylate.

37. General Properties.—In general, the terpenes are liquids that are practically insoluble in water, but to it they impart their characteristic tastes and odors. They are soluble in alcohol, ether, chloroform, benzene, petroleum ether, and as a rule, in all kinds of oils. All of the terpenes are volatile with steam and are optically active.

38. Classification.—With reference to their chemical compositions, the group $C_{10}H_{16}$ being taken as representative of the true terpenes, those hydrocarbons to which the name terpene is usually applied may be classified as follows: Hemiterpenes, C_5H_8; terpenes, $C_{10}H_{16}$; sesquiterpenes, $C_{15}H_{24}$; and polyterpenes, $(C_{10}H_{16})_x$. Another classification exists that is based on the structure of the terpene molecule. Thus, there are olefine terpenes, which are unsaturated, open-chain hydrocarbons; and cyclic terpenes, which are closed-chain, or ring, compounds.

HEMITERPENES

39. Isoprene, C_5H_8, the only hemiterpene of importance, is obtained by the dry or destructive distillation of either rubber or gutta percha. It is an unsaturated compound and, therefore, may be classed as an olefine terpene. Its structural formula is written as follows:



$$CH_2{:}\underset{\displaystyle CH_3}{\underset{|}{C}}{\cdot}CH{:}CH_2$$

Isoprene is a liquid that boils at 33.5° C., and has a specific gravity of .6804 at 21° C. It is insoluble in water but dissolves readily in alcohol and in ether. When isoprene is heated to about 300° C., during a period of several hours or when it is treated with sulphuric acid, it polymerizes with the formation of dipentene, $C_{10}H_{16}$, and colophene, $C_{20}H_{32}$. Under certain conditions, as when it is brought in contact with an acid, isoprene can be converted into rubber. On this reaction is based a laboratory process for the production of synthetic rubber. Up to the present, however, isoprene has not been produced cheaply enough to enable the rubber produced from it to compete with that obtained from natural sources.

TRUE TERPENES

40. Terpane and Camphane Groups.—The true terpenes, corresponding to the formula $C_{10}H_{16}$, are divided into two groups known as the terpane group and the camphane group. In the terpane group are included limonene, dipentene, phellandrene, sylvestrene, terpinolene, terpinene, and thujene. The members of this group boil between 175° and 185° C. and unite with two molecules of a halogen acid or with four atoms of bromine. The camphane group includes pinene, bornylene, camphene, and fenchene. These hydrocarbons boil between 151° and 161° C. and unite with one molecule of a halogen acid or two atoms of bromine.

41. Limonene, $C_{10}H_{16}$.—Limonene is known in three varieties; namely, *dextro*, *levo*, and *inactive* or *dipentene*. Dextro-limonene occurs in the oil obtained from the citrus fruits and in the oils of bergamot, oil of celery, etc. It boils at 175° C., and forms a tetrabromide of the formula $C_{10}H_{16}Br_4$, melting at 105° C. Levo-limonene occurs in the oil of fir, the oil of peppermint, and in the oil of fir needles. It also boils at 175° C. Both dextro and levo-limonene have the constitution represented by the formula shown in Fig. 15. They are liquids with an agreeable lemon-like odor, and a specific gravity of .846. They differ from each other, and this is true also of their derivatives, almost entirely by their opposite optical power. Dry hydrochloric acid converts them into the optically active hydrochlorides, while moist acid changes them into optically active addition products of dipentene. Exposure to high temperatures converts them into dipentenes. The constitution of the dextro- and levo-limonenes is inferred from their formation from terpineol by elimination of water, as shown in Fig. 16, and from the fact that the addition of two molecules of hydrobromic acid yields the same dibrom-

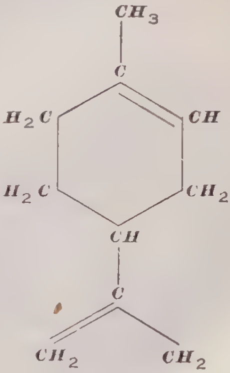
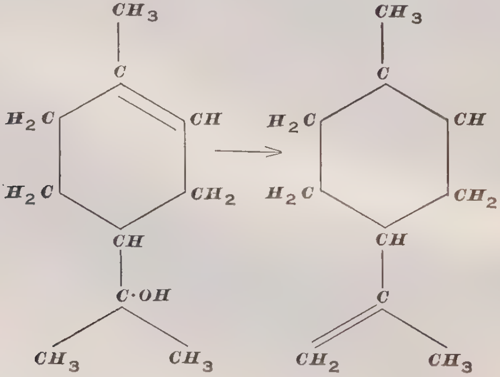


FIG. 15

menthane as is obtained from terpin by replacement of the hydroxyl groups by bromine.

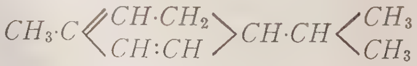
Dipentene, or *(d-+l-) limonene*, is prepared by heating the two optically active limonenes, by mixing these in equal proportions, and by heating pinene and camphene from 250° to 300° C. It is a constituent of Russian and Swedish oil of turpentine. It is a liquid with an agreeable lemon-like odor, has a specific gravity of .853, and is more stable than most of the other terpenes. Concentrated sulphuric acid oxidizes it to para-cymene.



terpineol d- and l-limonenes

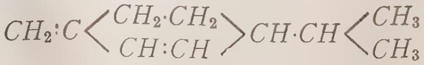
FIG. 16

42. Phellandrene, $C_{10}H_{16}$.—Phellandrene is found in the oils of eucalyptus, camphor, sassafras, etc. It exists as two structural isomerides designated as α-phellandrene and β-phellandrene and each of these isomers exists in two stereoisomeric modifications. Thus, there are dextro-α-phellandrene, levo-α-phellandrene, dextro-β-phellandrene, and levo-β-phellandrene. The structural formulas of the α and β modifications are written as follows:



$$CH_3{\cdot}C\left\langle\begin{array}{l} CH{\cdot}CH_2 \\ CH{:}CH \end{array}\right\rangle CH{\cdot}CH\left\langle\begin{array}{l} CH_3 \\ CH_3 \end{array}\right.$$

α-phellandrene



$$CH_2{:}C\left\langle\begin{array}{l} CH_2{\cdot}CH_2 \\ CH{:}CH \end{array}\right\rangle CH{\cdot}CH\left\langle\begin{array}{l} CH_3 \\ CH_3 \end{array}\right.$$

β-phellandrene

α-Phellandrene boils at 61° C., under a pressure of 11 millimeters and has a specific gravity of .844. β-Phellandrene boils at 57° C., under a pressure of 11 millimeters and has a specific gravity of .852.

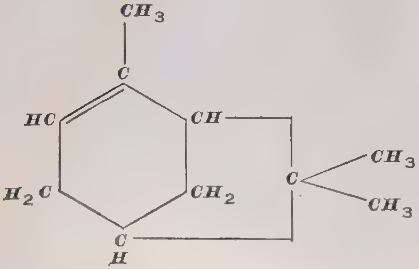
43. Sylvestrene and Thujene.—Both of the terpenes sylvestrene and thujene have the moecular formula $C_{10}H_{16}$. Sylvestrene is a constituent of the oils of turpentine of Swedish and Russian origin. It is a liquid having a specific gravity of .8492 at 16° C., and an odor similar to that of freshly cut pine wood. When a drop of concentrated sulphuric acid is added to a solution of sylvestrene in acetic anhydride, a blue color is produced. This test serves to distinguish sylvestrene from all other terpenes. Thujene is found in the essential oils of thuja and tansy. It boils at about 171° C., and has a specific gravity of .836. It yields a red color when a drop of concentrated sulphuric acid is added to its acetic anhydride solution. This test is characteristic and serves to distinguish it from other terpenes.

44. Terpinene and Teripnolene, $C_{10}H_{16}$.—Terpinene and terpinolene are produced by the action of concentrated sulphuric acid on phellandrene, dipentene, and other terpenes. Both are liquids that react with bromine and the halogen acids. Terpinolene tetrabromide is a solid that melts at 116° C.; the bromides of terpinene are liquids at ordinary temperatures.

45. Pinene, $C_{10}H_{16}$.—Pinene is the chief constituent of the various oils of turpentine, in which it exists in the three stereoisomeric modifications, dextro, levo, and inactive. The dextro variety is found chiefly in the American and English oils of turpentine and the levo variety in the French oil. Pinene is a colorless, transparent liquid soluble in alcohol, but scarcely soluble in water. It boils at 156° C., and has a specific gravity of .8587 at 20° C. When pinene is heated to 250° C. in a sealed tube it is converted into dipentene. The inactive pinene is formed by a combination of the dextro and levo varieties.

The structural formula of pinene may be written as shown in Fig. 17.

The presence of a double bond in pinene is proved by its combining with two atoms of chlorine or bromine and by the formation of pinene hydrochloride by the addition of one molecule of hydrochloric acid. This compound is called *artificial camphor*, and resembles camphor in both appearance and odor.



pinene
FIG. 17

46. Camphene, $C_{10}H_{16}$.—Camphene with the exception of bornylene is the only known solid terpene. It exists in three varieties: dextro, levo, and inactive. It is formed by heating borneol with potassium bisulphate, and by the action of sodium acetate and glacial acetic acid on pinene hydrochloride at 200° C.

Camphene melts at about 47° C., and boils at 159° C. It is insoluble in water but dissolves readily in alcohol and in ether.

47. Bornylene and Fenchene, $C_{10}H_{16}$.—Bornylene and fenchene do not occur naturally. The first is prepared from the terpene alcohol known as borneol and the second by reduction of a terpene ketone called fenchone.

Bornylene melts at 113° C. and boils at 146° C. It is insoluble in water but dissolves in alcohol and ether.

Fenchene boils at about 155° C. It does not dissolve in water but is extremely soluble in alcohol and ether.

SESQUITERPENES

48. The sesquiterpenes have the molecular formula $C_{15}H_{24}$. They are obtained from the essential oils of cedar wood, rosewood, patchouli, allspice, ginger, and cubebs. They differ from the true terpenes in several respects. Thus, they are viscous liquids that boil between 255 and 275° C. and are not polymerized by sulphuric acid

Two members of this class may be mentioned. They are cadinene, which is obtained from oil of patchouli. It has a specific gravity of .918 at 20° C., and boils at about 274° C.

Cedrene is obtained from oil of cedar wood. It has a specific gravity of .936 at 15° C. and boils at about 262° C.

POLYTERPENES

49. Little is known concerning the members of this class. They are formed by the polymerization of hemiterpenes and true terpenes. Thus, colophene, $C_{20}H_{32}$, is formed when sulphuric acid is brought in contact with oil of turpentine. It is a fluorescent liquid of high viscosity, that boils above 315° C.

Diterpilene, isomeric with colophene, is obtained by heating oil of turpentine with 100-per-cent. formic acid. It is a viscous liquid that does not rotate the plane of polarized light.

OXIDATION PRODUCTS OF TERPENES

UNSATURATED TERPENE ALCOHOLS

50. Geraniol, $C_{10}H_{17}OH$.—Geraniol is a monohydroxy, primary, open-chain alcohol, the structural formula for which is written, $(CH_3)_2C:CH \cdot CH_2CH_2 \cdot C \cdot CH_3:CH \cdot CH_2OH$. It is the principal constituent of the oils of geranium, palamarosa, and rose, but it also occurs in oil of citronella. Geraniol may be isolated from the well-dried oils that constitute its chief sources, by treating them with anhydrous calcium chloride, thus forming a crystalline compound having the formula $(C_{10}H_{17}OH)_2CaCl_2$.

Geraniol is a colorless oil having an odor like that of a rose. It is insoluble in water but very soluble in alcohol and ether, and has a specific gravity of .8812 at 16° C. It boils at 230° C. and is optically inactive.

51. Linalol, $C_{10}H_{17}OH$.—Linalol occurs naturally in oil of linaloe, of which it forms the chief constituent. It is a monohydroxy, open-chain alcohol, isomeric with geraniol, but is optically active and exists in both levo and dextro modifications. It is a colorless, oily liquid that has a specific gravity of .8622 at 20° C., and boils at 199° C. It is very slightly soluble in water but dissolves readily in alcohol and in ether.

52. Citronellol, $C_1H_{19}OH$.—Citronellol occurs in the oils of lemon, geranium, and rose. It is a monohydroxy, primary alcohol the formula for which is written, $C(CH_3)_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_3{\cdot}CH_2{\cdot}CH_2OH$. Citronellol is an oily liquid that boils at 222° C., and has a specific gravity of .8612 at 20° C. It is very slightly soluble in water but dissolves readily in alcohol and in ether.

CYCLIC TERPENE ALCOHOLS

53. Borneol, $C_{10}H_{17}OH$.—Borneol is a constituent of the borneol camphor found in cavities in trees of the *Dryobalonops aromatica* family, which grow in Borneo, Sumatra, the Sunda Islands, etc. It is obtained artificially by the reduction of ordinary camphor. The variety obtained from the natural sources is dextrorotatory, and that obtained from valerian oil is levorotatory. It occurs in small, colorless, prismatic crystals melting at 206° C. and boiling at 212° C. It has an odor of both camphor and pepper, is nearly insoluble in water, but readily soluble in alcohol and in ether. The reduction of the ordinary camphor forms both dextro and levo varieties. Nitric acid converts both of these varieties into ordinary camphor. That borneol is an alcohol is proved by the action of glacial acetic acid and of phosphorus pentachloride, the former yielding an acetate, according to the equation

$$C_{10}H_{17}{\cdot}OH + CH_3{\cdot}COOH = C_{10}H_{17}O{\cdot}CO{\cdot}CH_3 + H_2O$$

and the latter forms a chloride, according to the equation

$$C_{10}H_{17}{\cdot}OH + PCl_5 = C_{10}H_{17}Cl + POCl_3 + HCl$$

54. Terpineol and Pulegol, $C_{10}H_{17}OH$.—Terpineol occurs naturally in the oils of camphor, cardamom, and cajuput. It exists in three isomeric modifications, all of which are practically insoluble in water but very soluble in alcohol and in ether.

α-terpineol has a specific gravity of .9357 at 20° C., melts at 35° C., and boils at 218° C.

β-terpineol has a specific gravity of .923 at 15° C., melts at 32° C., and boils at 210° C.

γ-terpineol, as synthesized by Bayer, melts at 69° C.

Terpineol has an odor resembling that of the lilac flower and since it does not decompose on contact with alkalies or fatty acids, it is used as a perfume in the manufacture of toilet soaps.

Pulegol does not occur in nature but may be obtained by reduction of the ketone, pulegone. It has an odor like that of terpineol and boils at 215° C.

55. Menthol, $C_{10}H_{19}OH$.—Menthol, or mint camphor, is the solid part of the essential oil of peppermint. It crystallizes from the oil, on cooling, in colorless crystals soluble in alcohol and in ether, very slightly soluble in water and retaining the peppermint odor. It melts at 44.5° C. and boils at 215° C. Dehydrating agents convert it into *menthene*, $C_{10}H_{18}$.

Menthol is used in medicine as an antiseptic and is applied externally to relieve the pain of headache and other forms of neuralgia.

TERPENE ALDEHYDES

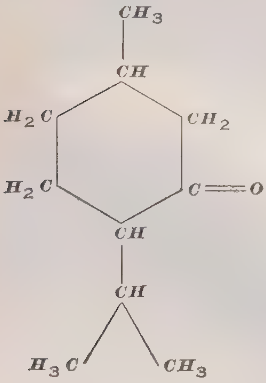
56. Citral, $C_9H_{15}CHO$.—Citral, geranial, or geranaldehyde, occurs to the extent of 70 to 80 per cent. in lemon-grass oil. It is an oily liquid, insoluble in water but very soluble in alcohol or in ether. Its specific gravity is .8868 at 20° C., and it boils at 228° C. It is optically inactive and on reduction is converted into geraniol. Citral is of importance because of its use as a starting point in the manufacture of certain synthetic perfumes.

57. Citronellal, $C_9H_{17}CHO$.—Citronellal is found chiefly in oil of citronella. Like citral, it is an oily liquid. It is only slightly soluble in water, but very soluble in alcohol and in ether. Its specific gravity at 17° C. is .8554. It boils at 206° C., and is dextrorotatory. On reduction, citronellal is converted into citronellol.

TERPENE KETONES

58. Introductory.—The terpene ketones are classified as open-chain and closed-chain, or cyclic, ketones, depending on the structure of the molecule. Many of these ketones occur naturally in the essential oils or they may be obtained by oxidation of the true terpenes. Among the open-chain ketones may be mentioned methyl heptyl ketone, $CH_3{\cdot}CO{\cdot}C_7H_{15}$, a liquid obtained from oil of rue and boiling at about 194° C.; and methyl nonyl ketone, $CH_3{\cdot}CO{\cdot}C_9H_{19}$, also obtained from oil of rue and boiling at 232° C.

The closed-chain or cyclic ketones include menthone, $C_{10}H_{18}O$; camphor, $C_{10}H_{16}O$; pulegone, $C_{10}H_{16}O$; fenchone, $C_{10}H_{16}O$; thujone, $C_{10}H_{16}O$; and carvone, $C_{10}H_{14}O$.



menthone

FIG. 18

59. Menthone.—Menthone occurs naturally in oil of peppermint. It is a liquid that has a specific gravity of .8972 at 20° C., and boils at 206° C. It is insoluble in water, but very soluble in alcohol, in ether, in carbon bisulphide, and in benzene. Its structural formula is written as shown in Fig. 18.

60. Camphor.—Camphor occurs naturally in the essential oil of camphor. Its chief source, however, consists of the leaves, twigs, and branches of the camphor tree (*Laurus* and *Cinnamomum camphora*), which is a native of Japan, China, and Formosa. It is obtained by steam distillation of the leaves, twigs, and branches, or they may be merely boiled with water, the solid camphor separating from the distillate or extract on cooling. The crude camphor thus obtained is refined by subliming it in the presence of lime and charcoal.

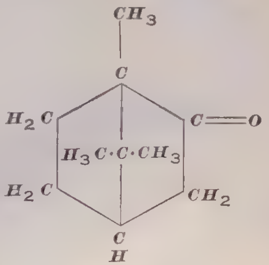
Pure camphor comes to the market in the form of cakes into which the sublimed product has been pressed. It melts at about 176° C., boils at 209° C., and has a specific gravity of

.963 at 20° C. It has a characteristic odor, is inflammable, and burns with a smoky flame. Camphor is only slightly soluble in water but dissolves readily in alcohol and in ether. It sublimes slowly at ordinary temperatures and if not kept in sealed containers, it gradually disappears. Natural camphor is dextrorotatory.

Camphor is a saturated ketone and does not form addition products Distilled with phosphorus oxychloride, it loses water and cymene is formed; thus,

$$C_{10}H_{16}O = C_{10}H_{14} + H_2O$$

The structure of the camphor molecule is represented as shown in Fig. 19.



camphor
FIG. 19

By far the greater quantity of the world's production of camphor is used in the manufacture of celluloid. A large quantity is also used in the manufacture of medicinal preparations, and some is incorporated with explosives to render them less sensitive to shock.

61. Synthetic Camphor.—Camphor may be made synthetically by the following process: Well-dried turpentine is first treated with dry hydrochloric acid gas (hydrogen chloride), at a low temperature, pinene hydrochloride being precipitated, which is converted, subsequently, into isobornyl acetate, $C_{10}H_{17}O{\cdot}CO{\cdot}CH_3$, by heating it with sodium acetate and acetic acid. The isobornyl acetate is then hydrolyzed by boiling with alcoholic sodium hydroxide and the borneol, $C_{10}H_{17}OH$, thus obtained is converted into camphor by oxidation with nitric or chromic acids.

Synthetic camphor is optically inactive, otherwise it is identical with the natural product, which is dextrorotatory.

The manufacture of synthetic camphor on a large scale has been successfully carried out in the United States. Under normal economic conditions, however, the synthetic product cannot compete with natural camphor, which is imported from Japan.

62. Pulegone, Fenchone, and Thujone.—The principal source of pulegone is oil of pennyroyal. It boils at 222° C., has a specific gravity of .9323 at 20° C., and though insoluble in water is very soluble in alcohol and in ether. Pulegone has an odor resembling that of peppermint. Fenchone and thujone are found together in oil of thuja. The most important source of fenchone, however, is oil of fennel.

Fenchone is a solid that melts at 8.5° C., boils at 192.5° C., and has a specific gravity of .9465 at 19° C. It is insoluble in water but dissolves readily in alcohol and in ether.

Thujone is a liquid that boils at 200° C., and has a specific gravity of .9126 at 20° C.

63. Carvone, $C_{10}H_{14}O$.—Carvone is found in the oils of caraway, fennel, and dill. It is a colorless, oily liquid that boils at 230° C., and has a specific gravity of .9608 at 20° C. Carvone is only slightly soluble in water but dissolves readily in alcohol and in ether. It is optically active and both levo and dextro forms are known. When carvone is heated with glacial acetic acid, it is converted into carvacrol.

PHENOLS AND PHENOLIC ETHERS

64. Introductory.—The principal phenols and phenolic ethers that occur with the terpenes in essential oils are thymol, $C_6H_3{\cdot}CH_3{\cdot}CH(CH_3)_2{\cdot}OH$; eugenol, $C_3H_5C_6H_3(OCH_3){\cdot}OH$; and safrol, $CH_2{\cdot}O_2{\cdot}C_6H_3CH_2{\cdot}CH{:}CH_2$. Thymol, the principal constituent of oil of thyme, has been treated in a preceding Section.

65. Eugenol and Safrol.—Eugenol is the chief constituent of oil of cloves, in which it occurs to the extent of 75 to 95 per cent. It may be obtained by treating the oil with a dilute solution of potassium hydroxide. The oil that remains is discarded and a current of carbon dioxide is passed through the alkaline solution to liberate the eugenol, or it may be set free by neutralizing the alkali with hydrochloric acid. The product thus obtained is washed free from acid and is then purified by distillation.

Eugenol is a colorless oil that possesses the odor and taste of cloves. It has a specific gravity of 1.0696 at 15° C. and boils at 253.5° C.; it is very slightly soluble in water but very soluble in alcohol and in ether.

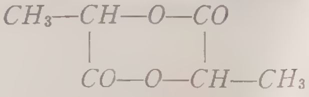
Safrol, the chief constituent of oil of sassafras, is also found in oil of camphor, from which it is obtained by fractional distillation and subsequent crystallization. At ordinary temperatures safrol is a colorless liquid having an odor like that of sassafras. When strongly chilled it solidifies, forming crystals that melt at about 11° C. Safrol has a specific gravity of 1.096 at 15° C., and boils at 233° C. It is insoluble in water but dissolves readily in alcohol and in ether. Safrol is used in perfumery and in the manufacture of heliotropine.

CYCLIC COMPOUNDS

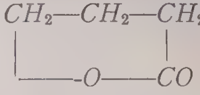
CLASSIFICATION

66. Before taking up the study of a new and important type of compound it will be advantageous to consider, for the purposes of classification, the different types of organic compounds studied thus far. The classification that will be used, in this instance, is based on the appearance of the graphic formula of the compound. Thus, it is well-known that an open-chain compound is one for which the graphic formula represents a straight or an open chain. In other words, no two atoms are connected in such a manner as to form a ring. The formula for ordinary butane, $CH_3—CH_2—CH_2—CH_3$, will serve as an illustration of this class.

67. The first closed-chain, ring or cyclic compound was met with when the lactides and lactones were studied. At this point it was shown that when an acid of the type of α-hydroxy acid loses one molecule of water, there is formed a lactide,



$$\begin{array}{ccccccccc} CH_3 & — & CH & — & O & — & CO & & \\ & & | & & & & | & & \\ & & CO & — & O & — & CH & — & CH_3 \end{array}$$

Again when a γ- or a δ-hydroxy acid is heated, water is lost and a lactone, such as butyrolactone,  $\begin{array}{l} CH_2-CH_2-CH_2 \\ \lfloor\quad -O-\quad CO \end{array}$, is formed. Probably a better illustration of a closed-chain, ring or cyclic type of compound is furnished by benzene, or a related compound, such as napthalene or anthracene.

The ring formulas given for the lactide and lactone, and for benzene, exhibit one difference on which is based a subdivision of the present classification. Thus, in the case of benzene, the ring consists solely of carbon atoms and it is designated as *homocyclic* or more definitely as *carbocyclic*. In the case of butyrolactone, however, one of the atoms in the ring is oxygen. Consequently, the compound is described as being *heterocyclic*. Organic compounds may then be arranged in the following classes:

1. Open-chain compounds.
2. Closed-chain, or cylic, compounds.
    - (*a*) Homocylic or carbocylic compounds:
        1. Alicyclic compounds
        2. Aromatic compounds
    - (*b*) Heterocyclic compounds.

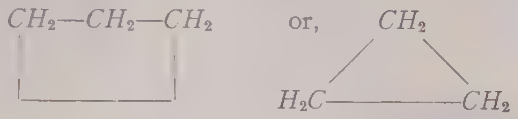
With the exception of the alicyclic and heterocyclic compounds, all of the foregoing have been treated.

ALICYCLIC COMPOUNDS

68. Introductory.—The alicyclic compounds, or the cycloparaffins, are those aliphatic or paraffin hydrocarbons and their derivatives the structures of which are represented by a closed chain, or ring. They are isomeric with the olefines and have the same general formula, C_nH_{2n}, but they are not unsaturated compounds and therefore do not yield addition products. They are more stable than the olefines and in their chemical and physical properties they resemble the paraffins.

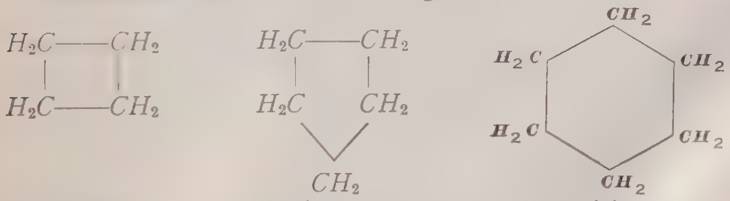
69. Cyclopropane, C_3H_6.—Cyclopropane or trimethylene is prepared by the action of metallic sodium on 1-3 dibrompropane or trimethylene bromide, $CH_2Br—CH_2—CH_2Br$: thus, $CH_2Br—CH_2—CH_2Br+2Na=(CH_2)_3+2NaBr$

If the assumption is kept in mind that carbon is tetravalent and that the compound formed by the foregoing reaction does not react as an unsaturated compound, it is evident that the formula for the reaction must take the form of a closed chain and can be written only as follows:



At ordinary temperatures, cyclopropane is a gas. The liquid boils at −34° C., under a pressure of 749 millimeters, and may be frozen to a solid that melts at −126° C. It is insoluble in water but is very soluble in alcohol and in ether.

70. Homologues of Cyclopropane.—The three members of the homologous series that follow cyclopropane are cyclobutane, or tetramethylene, C_4H_8; cyclopentane, or pentamethylene, C_5H_{10}; and cyclohexane, or hexamethylene, C_6H_{12}. They may be prepared by a method similar to that used for the preparation of cyclopropane. Their structural formulas are written as shown in Fig. 20.



cyclobutane cyclopentane cyclohexane

FIG. 20

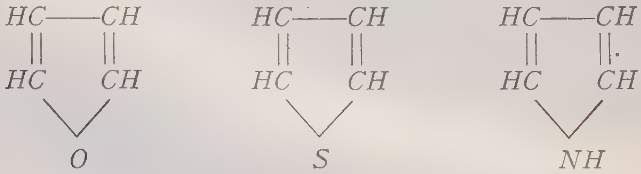
Cyclopentane is an oily liquid, insoluble in water, having a specific gravity of .7754 and boiling at 50° C.

Cyclohexane is a solid, insoluble in water but very soluble in alcohol and in ether. It has a specific gravity of .7791, melts at 6° C., and boils at 81° C. It has been treated in a preceding Section as a derivative of benzene, under the name of hexahydrobenzene.

HETEROCYCLIC COMPOUNDS

FIVE-MEMBERED RINGS

71. Introductory.—A few compounds, such as the lactones, which have already been described, although strictly belonging to the closed-chain, or cyclic, class of compounds, have more of the nature of open-chain derivatives. Their prototypes are found in the heterocyclic compounds furfuran, thiophen, and pyrrole, the structures of which are expressed by the formulas shown in Fig. 21.



furfuran thiophen pyrrole

Fig. 21

Most of the heterocyclic compounds that are directly related to benzene and that possess similar properties, contain either five or six atoms in the ring or they are made up of condensed rings and are of the type of naphthalene.

72. Furfuran.—Furfuran, or simply furan, is present in the distillation products of pine wood. It may be prepared by distilling barium pyromucate, $Ba(C_4H_3 \cdot O \cdot COO)_2$, with soda-lime or by heating pyromucic acid, $C_4H_3 \cdot O \cdot COOH$, at a temperature of 275° C.

Hydrogen is not evolved when furfuran is treated with metallic sodium nor does furfuran react with phenylhydrazine or hydroxylamine. These properties indicate that it contains neither a hydroxyl nor a carbonyl group and that the oxygen is linked to the remainder of the molecule as shown in the structural formula given. Furfuran is a liquid that boils at 32° C., and has a specific gravity of .9444 at 15° C. It is insoluble in water but dissolves readily in alcohol and in ether.

73. Furfural, Furfuryl Alcohol, and Pyromucic Acid. Furfural, furfuryl alcohol, and pyromucic acid have the structures represented by the formulas shown in Fig. 22.

Furfural, or as it is also known, furfurole or furfuraldehyde, is the most important derivative of furfuran. It is an aldehyde and is obtained by boiling bran or materials that contain sugars, such as xylose or arabinose, with dilute acids.

Furfural is a liquid that is slightly heavier than water, having a specific gravity of 1.1594 at 20° C. It boils at 161° C., and is soluble in water, in alcohol, and in ether. When freshly distilled, it is a colorless or bright-yellow liquid. On standing, however, its color changes to a dark yellow or a brown. On reduction, furfural yields furfuryl alcohol, and on odxidation, pyromucic acid. Furfuryl alcohol has a specific gravity of 1.1351 at 20° C., and boils at 170° C. It is a syrupy liquid that is soluble in water, in ether, and in alcohol.

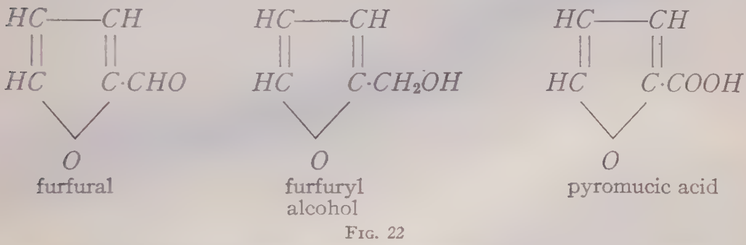


FIG. 22

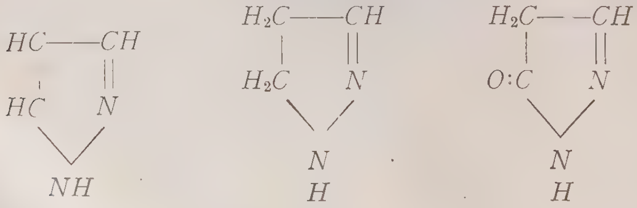
Pyromucic acid is a crystalline solid that melts at 132° C., and sublimes above 100° C. It is soluble in water, in alcohol, and in ether. In its chemical behavior it more nearly resembles the unsaturated aliphatic acids than it does those of the aromatic series. It yields a sulphonic acid, however, when treated with fuming sulphuric acid and in this respect resembles an aromatic compound.

74. Thiophen.—Thiophen is found with the hydrocarbons obtained from coal tar. It was discovered by Victor Meyer, who noticed the differences in the behavior of the benzene obtained from coal tar and that made from benzoic acid, when each was brought in contact with isatin. Thus, the coal tar benzene yields a blue color with isatin, the reaction by which it is produced being known as the indophenin reaction. Benzene made from benzoic acid does not yield the blue color and it was concluded that the reaction, in the case of coal-tar benzene, was due to the presence of an impurity. This impurity was isolated and the name of thiophen was given it.

Thiophen may be prepared by heating a mixture of sodium succinate and phosphorus trisulphide. It is a colorless liquid having a specific gravity of 1.0705 at 15° C. It boils at 84° C. and is insoluble in water but soluble in alcohol and in sulphuric acid.

75. Pyrrole.—Pyrrole owes its name to the fact that it imparts a red color to a pine shaving that has been moistened with hydrochloric acid. It occurs naturally in bone oil or Dippel's oil and in coal tar. It may be obtained by distilling succinimide, $(CH_2CO)_2NH$, with zinc dust.

Pyrrole is a colorless liquid turning brown on exposure to the air and light. It has an odor resembling that of chloroform, has a specific gravity of .9752, is insoluble in water, but mixes readily with alcohol and with ether. It boils at 131° C.



pyrazole pyrazoline pyrazolone

FIG. 23

Among the properties of pyrrole that indicate its relation to the aromatic compounds is its behavior with halogens. It yields substitution products but no addition products.

76. Pyrazole, Pyrazoline, and Pyrazolone.—Pyrazole, pyrazoline, and pyrazolone have the structures represented by the formulas shown in Fig. 23.

Pyrazole is obtained by the action of hydrazine on such compounds as propiolaldehydeacetal, $CH{:}C{\cdot}CH(OC_2H_5)_2$, and epichlorhydrin, $(CH_2)_2CH\cdot O\cdot Cl$. It is a crystalline compound that is very soluble in water, in alcohol, and in ether. It melts at 70° C. and boils at 187° C. Pyrazoline is obtained by the action of hydrazine hydrate on acrolein. It is soluble in water and alcohol and boils at 144° C. Its ketonic derivative is called pyrazolone, and some very important derivatives of this compound are obtained by the interaction of ethyl acetoacetate and phenyl hydrazine.

77. Antipyrine, $C_{11}H_{12}N_2O$.—Antipyrine, or dimethyl phenyl pyrazolone, is formed by the reaction that takes place between ethyl acetoacetate and phenyl hydrazine. The structure of antipyrine is represented by the formula shown in Fig. 24. It is a crystalline compound that melts at 113° C. It is very soluble in water but only slightly soluble in ether. An aqueous solution of antipyrine gives a red coloration with ferric chloride and a bluish-green coloration with nitrous acid. It is used extensively in medicine as a preventive of fever.

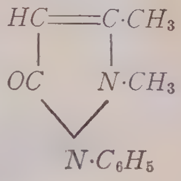


FIG. 24

SIX-MEMBERED RINGS

78. Pyridine, C_5H_5N.—Pyridine is produced by the dry distillation of nitrogenous substances. It is found in coal tar, in the tar obtained from certain bituminous shales, and in Dippel's oil, which is obtained by the dry distillation of bones.

$C_6H_5N\cdot H$
$C_6H_5\text{—}N\cdot$
$C_6H_5\text{—}N\cdot H$

Pyridine is a liquid with a characteristic and very disagreeable odor. Its specific gravity is .9746 at 25° C., it boils at 116° C., and is soluble in water and in alcohol. It has basic properties and forms salts with the acids.

Pyridine is used as a denaturant for alcohol and is employed as a solvent in the rubber and paint industries.

79. Homologues of Pyridine.—The formation of pyridine and its homologues, by the distillation of bones is due to the presence of ammonia (albumin), acrolein, methylamine, etc., and their action on each other at high temperatures. Members of the series are formed when aliphatic aldehydes are heated with ammonia, and pyridine and picoline are formed by the distillation of glycerol with ammonium sulphate and sulphuric acid.

All of the homologues of pyridine are liquids at ordinary temperatures, have an extremely disagreeable odor, and, being substituted ammonias, belong to the class of tertiary amines.

TABLE II

HOMOLOGUES OF PYRIDINE

Name	Empirical Formula	Boiling Point Degrees C.
Pyridine	C_5H_5N	115
Picoline	C_6H_7N	130
Lutidine	C_7H_9N	142
Collidine	$C_8H_{11}N$	179
Parvoline	$C_9H_{13}N$	188
Coridine	$C_{10}H_{15}N$	211
Rubidine	$C_{11}H_{17}N$	230
Viridine	$C_{12}H_{19}N$	251

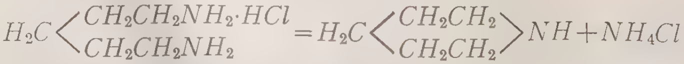
They are separated by fractional distillation. The various members of the series with their empirical formulas and melting points are given in Table II.

80. **Piperidine,** $C_5H_{11}N$.—Piperidine, or hexahydropyridine, occurs naturally in pepper, as an amide of piperic acid, $C_{10}H_7CH_2O_2 \cdot COOH$. It is synthetically prepared by the action of sodium on an alcoholic solution of pyridine, the latter taking up six atoms of hydrogen; thus,

$$C_5H_5N+6H=C_5H_{11}N$$

$6Na + 6C_2H_5OH = 6C_2H_5ONa + 6H$

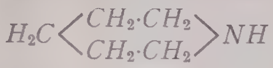
It is prepared also by the dry distillation of pentamethylenediamine hydrochloride; thus,



$$H_2C\left<\begin{matrix}CH_2CH_2NH_2 \cdot HCl\\ CH_2CH_2NH_2\end{matrix}\right. = H_2C\left<\begin{matrix}CH_2CH_2\\ CH_2CH_2\end{matrix}\right>NH+NH_4Cl$$

Piperidine is a colorless liquid with an odor of pepper and ammonia, and a caustic taste. It is miscible with water and with alcohol, has a specific gravity of .875, and boils at 106° C. It is a strong base and forms salts with the acids.

81. Structures of Piperidine and Pyridine.—Piperidine, as has been stated, is formed when pentamethylenediamine hydrochloride is distilled, and since ammonium chloride is the only other compound formed by the reaction, it is evident that piperidine has the structure represented by the formula



$$H_2C{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}NH$$

Again, when pyridine is acted on by nascent hydrogen, piperidine is formed and when the latter is subjected to the action of oxidizing agents, pyridine is obtained. In other words, pyridine results when six atoms of hydrogen are removed from piperidine. Consequently, pyridine has the structure represented by the formula shown in Fig. 25.

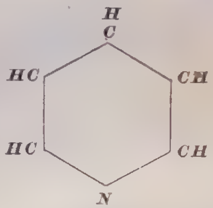


FIG. 25

CONDENSED HETEROCYCLIC COMPOUNDS

82. Indole, C_8H_7N.—Indole is obtained by the distillation of indigo with zinc dust. It has the structural formula shown in Fig. 26. This formula indicates that it is made up of a benzene nucleus condensed with a pyrrole nucleus. It is a decomposition product of the pancreatic digestion, being formed by the breaking up of albuminoid substances.

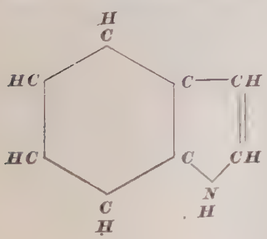


FIG. 26

It forms colorless to yellowish scales having a disagreeable odor. It is soluble in alcohol, ether, and hot water, melts at 52° C., and boils at 254° C. with partial decomposition. Highly dilute solutions of indole have an odor of orange blossoms. It is a very weak base, and gives a red coloration with hydrochloric acid.

83. Skatole, C_9H_9N.—Skatole, or methyl indole, has the structure represented by the formula, shown in Fig. 27.

It occurs naturally in a species of wood grown in India. It is formed by the decay of albuminoids and can be prepared by fusing egg albumin with caustic potash. It forms white to brownish, thin, shining scales that have a very disagreeable odor. Skatole is soluble in hot water, in alcohol, and in ether. It melts at 95° C., and boils at 265° C.

84. Quinoline, C_9H_7N.—Quinoline is found in bone oil and in coal tar. It may be prepared by distilling such substances as quinine and strychnine, with caustic potash. It is best prepared, however, by Skraup's synthesis, which consists in heating a mixture of glycerol, aniline, sulphuric acid, and nitrobenzene. In the reaction that takes place, the glycerol is first converted into acrolein, which in turn reacts with the aniline to form acrylaniline, $C_6C_5N{:}CH{\cdot}CH{\cdot}CH_2$. The latter is then oxidized by the nitrobenzene to quinoline; thus,

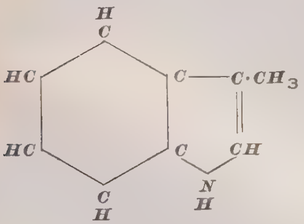


FIG. 27

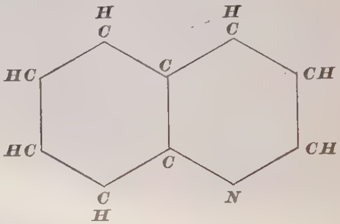


FIG. 28

$$CH_2{:}CH{\cdot}CHO + C_6H_5NH_2 = C_6H_5N{:}CH{\cdot}CH{:}CH_2 + H_2O$$
$$C_6H_5N{:}CH{\cdot}CH{:}CH_2 + O = C_9H_7 + H_2O$$

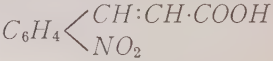
The structure of quinoline is represented by the formula shown in Fig. 28, which indicates that it is made up of a benzene and a pyridine nucleus.

INDIGO

NATURAL INDIGO

85. Indigo, $C_{16}H_{10}N_2O_2$. probably the oldest and one of the most important dyes in use today, occurs naturally as the colorless glucoside, indican, principally in the leaves and juice of the indigo plant, *Indigofera tinctoria*, which is cultivated in the tropical countries, Bengal, India, Java, and China, and in Central America. It is obtained from the plant by allowing the latter to stand in tanks in contact with warm water. Under these conditions an enzyme present in the plant causes fermentation to take place, which results in the hydrolysis of the indican present. The products of hydrolysis are glucose and the soluble, colorless leuco base of indigo, which is known as indigo white. When fermentation is complete, the solution is drawn off to other tanks and aerated by agitation. In this way the soluble leuco base is oxidized and the insoluble blue dye, indigo, is precipitated. After separation of the latter by filtration, it is pressed in the form of cubes or irregular lumps, then dried and sent to the market. Solid indigo blue is a dusty, chalky material which, when polished, exhibits a copper-like lustre. At the present time comparatively little natural indigo finds its way to the market, its place having been taken by synthetic indigo.

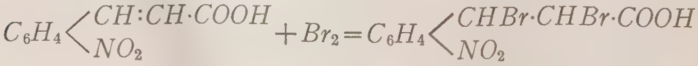
SYNTHETIC INDIGO

86. Baeyer's Synthesis of Indigo.—Natural indigo contains as impurities substances that are now known as indirubin, or indigo red, indigo brown, indigo yellow, and indigo gluten. The valuable constituent of natural indigo is called indigo blue or indigotin, and it was the synthesis of this substance that was the goal of all those investigators whose names are identified with the history of synthetic indigo. Early in the 19th century it was shown that distillation of indigo with caustic potash produced aniline, $C_6H_5NH_2$, and that anthranilic acid, $C_6H_4\cdot NH_2\cdot COOH$, was formed when indigo was fused with caustic potash. It was also discovered about this time that on oxidation of indigo the compound known as isatin, $C_8H_5NO_2$, was produced. Since isatin is one of the oxdiation products of indigo, the German chemist, Adolph Baeyer, naturally assumed that by reducing isatin he would obtain indigo. He failed to accomplish this object at this time, however, but in the course of his work, he, with another chemist, Knop, discovered the compounds dioxindole, $C_8H_7NO_2$, oxindole, C_8H_7NO, and indole, C_8H_7N, as the successive reduction products of isatin. It was Baeyer's belief that indole was the mother substance of indigo and in conjunction with Emmerling he was able, in 1869, to prepare it synthetically by heating ortho-nitrocinnamic acid,  $C_6H_4\left\langle\begin{matrix}CH{:}CH\cdot COOH\\ NO_2\end{matrix}\right.$ with caustic potash and iron filings.

87. In 1870, Baeyer and Emmerling prepared indigo by heating isatin with a mixture of phosphorus trichloride and acetyl chloride. The next problem to be solved in the preparation of synthetic indigo was then the synthesis of isatin. This was accomplished by Baeyer in 1880 by modifying the method that he had used for the synthesis of indole. The composition of indigo may be represented by the empirical formula C_8H_5NO, and apparently the removal of carbon dioxide and water from ortho-nitrocinnamic acid should yield indigo; thus,

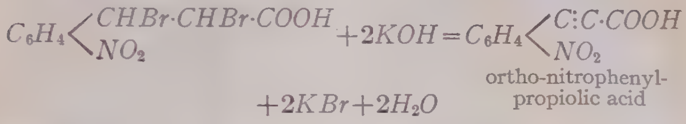
$$\underbrace{C_8H_5H_2O\cdot NO\cdot CO_2}_{\text{ortho-nitrocinnamic acid}}-(H_2O+CO_2)=C_8H_5NO$$

In the experimental work that followed, carbon dioxide was easily removed from the acid but it was found impossible to remove the hydrogen and oxygen as water. Therefore it was necessary to resort to an indirect method to effect this result. When bromine reacts with ortho-nitrocinnamic acid, the compound obtained is dibromnitrohydrocinnamic acid; thus,



$$C_6H_4\left\langle\begin{matrix}CH{:}CH\cdot COOH\\ NO_2\end{matrix}\right.+Br_2=\underbrace{C_6H_4\left\langle\begin{matrix}CHBr\cdot CHBr\cdot COOH\\ NO_2\end{matrix}\right.}_{\text{dibromnitrohydrocinnamic acid}}$$

Hydrobromic acid was then removed from the bromine compound by means of alcoholic potash, the result being a new acid called ortho-nitrophenylpropiolic acid, which contains two less hydrogen atoms; thus,



$$C_6H_4\left\langle\begin{matrix}CHBr\cdot CHBr\cdot COOH\\ NO_2\end{matrix}\right. + 2KOH = \underset{\text{ortho-nitrophenyl-propiolic acid}}{C_6H_4\left\langle\begin{matrix}C{:}C\cdot COOH\\ NO_2\end{matrix}\right.} + 2KBr + 2H_2O$$

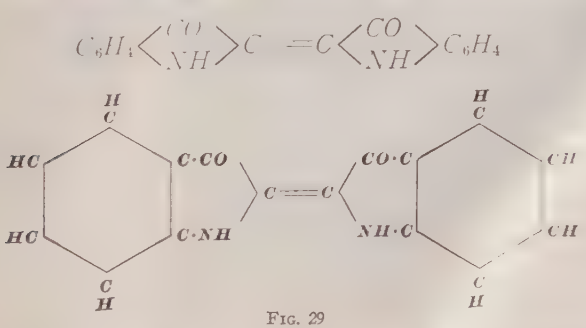
When the formula for this acid is reduced to the empirical form, $C_8H_5\cdot NO_2\cdot CO_2$, it is seen that it contains one more molecule of carbon dioxide than does isatin and one more molecule of carbon dioxide and one more atom of oxygen than does indigo; thus,

$$C_8H_5\cdot NO_2\cdot CO_2 - CO_2 = \underset{\text{isatin}}{C_8H_5NO_2}$$

$$C_8H_5\cdot NO_2\cdot CO_2 - (CO_2 + O) = \underset{\text{indigo}}{C_8H_5NO}$$

In order to obtain isatin from the acid, Baeyer boiled it with caustic potash, by which means carbon dioxide was removed. In another experiment glucose was used with the caustic potash to remove oxygen by reduction and he succeeded in producing indigo.

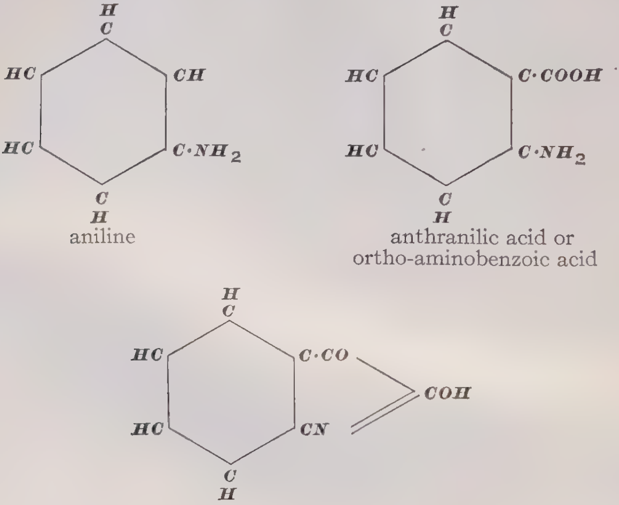
88. The investigations of Baeyer and his associates that have been described were carried out during a period of fifteen years. It was thought at first that the process could be used for the manufacture of indigo on a commercial scale



$$C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle C = C\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle C_6H_4$$

FIG. 29

but this did not prove to be the case, for the reason that the yields of ortho-nitrocinnamic acid, ortho-nitrophenylpropiolic acid, and consequently of indigo itself, were too small, thereby making the cost of the product too high to compete with natural indigo.



aniline

anthranilic acid or
ortho-aminobenzoic acid

isatin

Fig. 30

89. Structure of Indigo.—In the foregoing description of Baeyer's synthesis, the empirical formula C_8H_5NO has been used to represent indigo. The formula is correct as far as it goes, but determinations of the molecular weight of indigo indicate that it must consist of $(C_8H_5NO)_2$, and consequently the molecular formula should be written, $C_{16}H_{10}N_2O_2$. The structure of the indigo molecule as developed up to the present time is represented by either of the formulas shown in Fig. 29.

This formula for indigo is based on the structures of the products obtained when indigo is decomposed and on the reactions involved when it is synthesized by different methods. Thus, the presence of the benzene nucleus is indicated by the formation of aniline and anthranilic acid when indigo is heated and fused with caustic potash, and the formation of isatin when indigo is oxidized. The structures of these compounds are represented by the formulas shown in Fig. 30. In addition, these formulas indicate that in indigo, carbon and nitrogen may be linked to the nucleus in the ortho position as shown in Fig. 31.

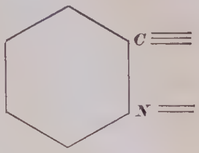
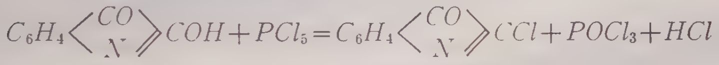


FIG. 31

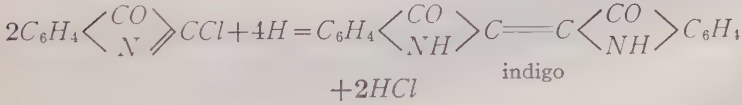
The foregoing discussion, with the exception of the theory concerning the exact structure of isatin, represents practically all that was known concerning the structure of indigo prior to the investigations of Baeyer and his associates, begun in 1865. The structure of isatin was established by Claisen and Shadwell in 1879.

90. When isatin is treated with phosphorus pentachloride, isatin chloride is formed, which, on reduction, yields indigo. The reactions involved indicate that indigo consists of two $C_6H_4\left\langle\begin{matrix}CO\\N\end{matrix}\right\rangle C-$ groups linked together. Thus,



$$C_6H_4\left\langle\begin{matrix}CO\\N\end{matrix}\right\rangle COH+PCl_5=C_6H_4\left\langle\begin{matrix}CO\\N\end{matrix}\right\rangle CCl+POCl_3+HCl$$

isatin isatin chloride



$$2C_6H_4\left\langle\begin{matrix}CO\\N\end{matrix}\right\rangle CCl+4H=C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4+2HCl$$

indigo

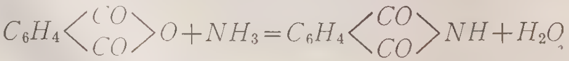
That the two isatin molecules are linked by a double bond between two of the carbon atoms is evident from the fact that ortho-dinitrodiphenyldiacetylene, $C_6H_4\left\langle\begin{matrix}C{:}C & - & C{:}C\\NO_2 & & NO_2\end{matrix}\right\rangle C_6H_4$, which contains the isatin nucleus, can be converted into indigo by treatment with sulphuric acid and subsequent reduction of the product formed. Thus, fuming sulphuric acid converts ortho-dinitrodiphenyldiacetylene into an isomeric compound called di-isatogen, which is represented by the formula $C_6H_4\left\langle\begin{matrix}CO\cdot C\cdot C\cdot CO\\ \mid \quad \mid \\ N\cdot O \quad O\cdot N\end{matrix}\right\rangle C_6H_4$. This compound on reduction yields indigo, $C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4$.

91. Heumann's Synthesis of Indigo.—The methods for the preparation of synthetic indigo that have been described and many others that were developed in the laboratory did not prove to be suitable for large-scale production because of the high cost of the indigo produced by them. In 1890, however, Heumann made public the results of his experiments to produce indigo. He had discovered that phenylglycine, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}COOH$, and phenylglycine ortho-carboxylic acid, $C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}(COOH)_2$, when fused with caustic potash, are converted into indoxyl and indoxylcarboxylic acid, respectively, and that these compounds when subsequently oxidized by the oxygen of the air are converted into indigo. These reactions were eventually to become the basis of the present commercial process for the synthesis of indigo. Before Heumann's reactions became of practical importance, however, it was necessary to find and develop a cheap and practically unlimited source of phenylglycine ortho-carboxylic acid. This source was found in naphthalene and the reactions involved in its conversion into phenylglycine ortho-carboxylic acid are enumerated and represented as follows:

On oxidation with sulphuric acid in the presence of mercury or mercuric sulphate, naphthalene yields ortho-phthalic acid,

$$\underset{\text{naphthalene}}{C_{10}H_8}+9H_2SO_4=\underset{\text{ortho-phthalic acid}}{C_6H_4(COOH)_2}+9SO_2+2CO_2+10H_2O$$

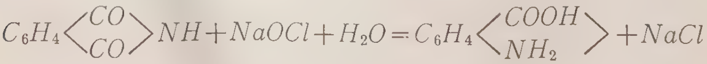
On heating ortho-phthalic acid, phthalic anhydride, $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O$, is formed by the loss of one molecule of water. Phthalic anhydride is then converted into phthalimide by the action of ammonia,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O+NH_3=C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH+H_2O$$

phthalimide

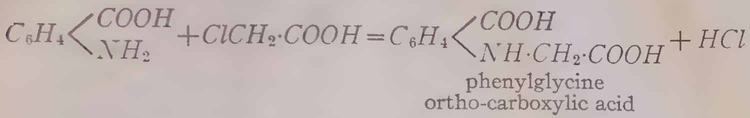
On treatment of the phthalimide thus obtained, with sodium hypochlorite, anthranilic acid is produced,



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH+NaOCl+H_2O=C_6H_4\left\langle\begin{matrix}COOH\\NH_2\end{matrix}\right\rangle+NaCl+CO_2$$

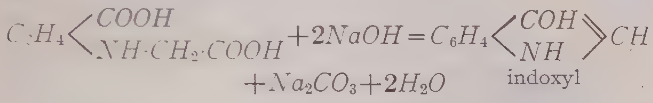
anthranilic acid

which when brought in contact with monochloacetic acid, forms phenylglycine ortho-carboxylic acid,

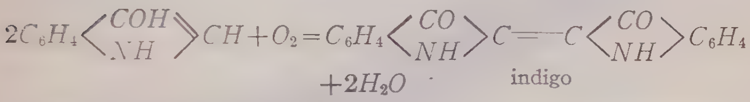


$$C_6H_4\left\langle\begin{matrix}COOH\\NH_2\end{matrix}\right. + ClCH_2\cdot COOH = \underset{\text{phenylglycine ortho-carboxylic acid}}{C_6H_4\left\langle\begin{matrix}COOH\\NH\cdot CH_2\cdot COOH\end{matrix}\right.} + HCl$$

This acid on fusion with the caustic alkalies yields indoxyl, which, in contact with atmospheric oxygen, is converted into indigo; thus,



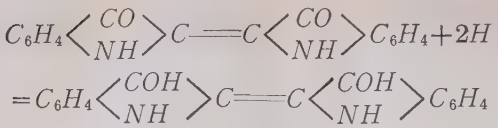
$$C_6H_4\left\langle\begin{matrix}COOH\\NH\cdot CH_2\cdot COOH\end{matrix}\right. + 2NaOH = \underset{\text{indoxyl}}{C_6H_4\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle CH} + Na_2CO_3 + 2H_2O$$



$$2C_6H_4\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle CH + O_2 = \underset{\text{indigo}}{C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4} + 2H_2O$$

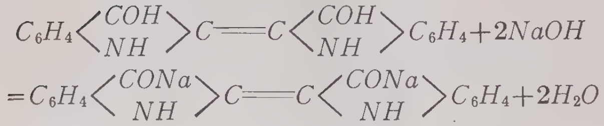
92. Vat Dyes.—Indigo belongs to that class of dyes known as vat dyes. In this class are included those dyes that are insoluble in water and in dilute solutions of the alkalies and acids, but which are easily reduced to closely related compounds that are soluble in dilute solutions of the alkalies. With vat dyes the color is developed on the fabric and not in the dye bath itself, as was the case with the dyes previously described. Indigo is probably the most important of the vat dyes and the processes employed in fixing it to the various textiles are typical for the dyes of this class. These processes involve a reduction of the indigo, in suitable vats, by means of nascent hydrogen, to the leuco base or colorless indigo white. An alkali is also present in the vat and it dissolves the leuco base. The solution is then brought in contact with the fiber and after thorough saturation of the latter, the excess solution is removed and on subsequent exposure of the fiber to the air, the leuco base is oxidized and indigo is reformed on the fiber itself.

The reduction of indigo to indigo white, the reaction that takes place when the indigo white is dissolved by an alkali, and the subsequent oxidation of the alkali salt of indigo white, may be represented by the following equations:



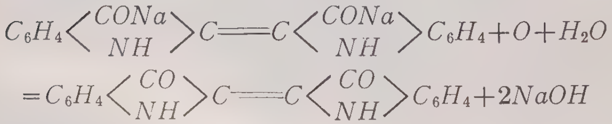
$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4+2H$$
$$=C_6H_4\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle C_6H_4$$

indigo white



$$C_6H_4\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}COH\\NH\end{matrix}\right\rangle C_6H_4+2NaOH$$
$$=C_6H_4\left\langle\begin{matrix}CONa\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}CONa\\NH\end{matrix}\right\rangle C_6H_4+2H_2O$$

sodium salt



$$C_6H_4\left\langle\begin{matrix}CONa\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}CONa\\NH\end{matrix}\right\rangle C_6H_4+O+H_2O$$
$$=C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C{=}C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4+2NaOH$$

indigo

Vat dyeing possesses a great advantage over other methods in that it is not necessary to use a mordant. Again, because of the insolubility of the dye as fixed on the fiber, it is very fast to washing and to sunlight.

$C_2H_5\text{-}OH + HCl = C_2H_5\text{-}Cl + H_2O$